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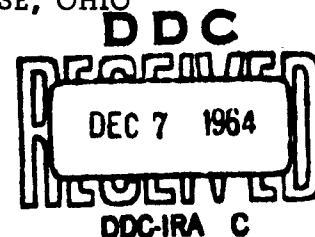FIRE PROTECTION RESEARCH PROGRAM

FOR SUPERSONIC TRANSPORT

Technical Documentary Report No. APL TDR-64-105

October 1964

Supersonic Transport Research Program
Sponsored by the
Federal Aviation Agency

AIR FORCE AERO PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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FOREWORD

ABSTRACT

The problems associated with flight fires in supersonic transport aircraft include most of the factors present in conventional aircraft as well as some additional problems caused in part by the high temperatures produced by supersonic flight and new design concepts. The possibility that the major fuel storage areas may be in the fuselage poses problems different from those associated with conventional wing tanks.

This study consists of three parts: (1) A summary of the environmental factors associated with the supersonic transport which affect the fire hazard problem and the problem of fire protection; (2) A summary of existing technical data pertinent to fire hazards and fire protection and interpretations of these data in terms of the supersonic transport; and (3) Formulation of a research program to provide the technical information not currently available and deemed necessary for an adequate understanding of the supersonic transport fire hazard problem and the associated problem of fire protection.

BLACKWELL C. DUNNAM
Chief, Support Techniques Branch
Technical Support Division
AF Aero Propulsion Laboratory

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SUMMARY

A comprehensive review of environmental and combustion data pertinent to the assessment of fire hazards associated with the supersonic transport has been conducted. Data and correlations have been presented which permit the calculation of the effect of the supersonic transport environment on the principal hazard parameters.

While many of the hazard factors are similar to those of subsonic aircraft, differing only in the relative magnitude of individual parameters, several problems are unique to the temperature and pressure environment of the supersonic transport.

The high temperature level associated with the supersonic cruise condition introduces the possibility of pre-flame oxidation and cool flame phenomena in regions where contact between flammables and air exists either normally as in fuel tanks or as the result of leakage or a damage configuration. These pre-flame oxidation and cool flame phenomena are not associated with the environment of subsonic aircraft. The possible hazards associated with oxidation and cool flames are discussed as well as the factors which affect the transition from these phenomena to normal flames or explosions. The need for further research to determine methods of minimizing the hazards associated with pre-flame oxidation and cool flames is emphasized including research on inhibitors, the use of inerting atmospheres and a more precise definition of the regions of hazard.

There is also a need for further research on the effects of fuel temperature, surface effects, additives and mixture composition on spontaneous ignition temperature. Various techniques appear possible to raise the spontaneous ignition temperature but adequate data are not available to assess the efficacy of such techniques. Isolation of components likely to leak flammable fluids might be accomplished if reasonable measures could assure that escaping fluid did not encounter a surface temperature sufficiently high to cause ignition. Several methods are discussed in the text.

The problems associated with selecting extinguishing agents suitable for use in a high temperature environment are also discussed. The specific problems of thermal stability and high fluid pressures are the major areas of concern. Halogenated hydrocarbons of adequate thermal stability have been investigaged but such compounds are often associated with poor low temperature viscosity behavior or high fluid system pressure. Isolating the driver gas and extinguishant is discussed as one means of lowering extinguishing system pressure. There is a need for further work on extinguishants and extinguishing systems before a completely satisfactory solution can be presented. The question of reactivity between halogenated hydrocarbons

and titanium should also be resolved although there is no positive evidence that titanium would be more reactive than metals such as magnesium.

The major voids in existing knowledge pertinent to the supersonic transport tire hazard problem are summarized. Some of the most significant of these were discussed above.

I. INTRODUCTION

The problems associated with flight fires in supersonic transport aircraft include most of the factors present in conventional aircraft as well as some additional problems not present on subsonic aircraft. These new problem areas arise in part from the high temperatures produced by supersonic flight through the atmosphere as well as from new design concepts which affect fire hazards. The possibility that the major fuel storage areas may be in the fuselage for a supersonic transport, for example, poses problems which differ from those associated with wing tanks in conventional subsonic aircraft. The problem areas relative to fire hazards associated with supersonic transports have not been defined nor is there a clear understanding of the advanced technical data required to evaluate the problem and suggest remedies.

It was the objective of this study to:

1. Summarize the environmental factors associated with the supersonic transport pertinent to the fire hazard problem and the problem of fire protection.

2. Summarize existing technical data pertinent to fire hazards and fire protection and interpret these data in terms of the supersonic transport.

3. Formulate a research program to provide the technical information not currently available and deemed necessary for an adequate understanding of the supersonic transport fire hazard problem and the associated problem of fire protection.

The emphasis of the study reported here is directed toward in-flight fires. The problem of crash fires associated with the supersonic transport was the subject of an independent study and had been reported previously (Ref 1).

II. TECHNICAL DISCUSSION

A. INTRODUCTION

The technical discussion is concerned with the summary of available knowledge pertinent to the supersonic transport environment and to the evaluation of fire hazards and fire protection.

In order to facilitate presentation of the material, the technical discussion has been sub-divided into the following major categories:

1. Aircraft Environment
2. Fluid Properties
3. Combustion Properties
4. Analysis of Hazards

B. AIRCRAFT ENVIRONMENT

The principal factors involved in the relationship of the aircraft environment to fire hazard potential are:

1. Temperature
2. Pressure
3. Air Flow
4. Geometry

These factors are discussed in the following section for typical flight conditions and selected hazard situations.

1. Flight Plan

The principal factor which determines the environment of the aircraft is the flight plan as it is related to the temperature and pressure of the surroundings as well as internal and external surfaces within the aircraft.

The most widely quoted flight plans for a Mach 3 supersonic transport involve minor variations of one plan. A reasonable representation of the generally used flight plan is shown in Figure 1 based on data cited in Ref 2. The flight plan consists of a 3500 nautical mile journey with a cruising altitude of 70,000 to 80,000 feet. In general, the climb and acceleration portion of the flight involve about 20 minutes and the descent and deceleration about 30 minutes. An important aspect of the flight plan is that speeds above Mach 1 are not reached below an altitude of about 45,000 feet, a factor which strongly affects the temperature history of the aircraft.

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Flight Mach numbers below 3, varying from 2.2 to 3, have been suggested for the supersonic transport. It is not unreasonable to assume, for the purposes of this report, that the flight plan would be quite similar to that shown in Figure 1 except that the cruise Mach number would be lower. The effects of the lower cruise Mach number on fire hazard potential will be discussed in other sections of the report.

2.   Temperature

The temperature of most of the aircraft surface is determined by flight Mach number and altitude. These temperatures are modified at certain locations within the aircraft. Heat sinks such as the fuel and various cooling systems produce areas of relatively low temperature. Heat sources such as the engine, electrical components, etc. produce local areas of relatively high temperature.

   a. Ambient Air Temperature

The temperature of the air remote from the aircraft is determined by the altitude at which the aircraft is operating. A graph for the standard variation of ambient temperature with altitude is given in Figure 2, from data of Ref 3.

The temperature which the aircraft skin experiences will be a function of the ambient temperature, the flight Mach number and a recovery factor which determines the fraction of the kinetic energy of the moving air which has been converted to heat.

   b. Stagnation Temperature

The maximum temperature to which the aircraft is exposed during flight, often called the stagnation temperature, occurs when the kinetic energy of the air has been converted to heat with no losses. The stagnation temperature ratio to the ambient temperature as a function of Mach number is given by the equation (Ref 4)

$$\frac{T_s}{T_a} = 1 + \frac{\gamma - 1}{2} M^2 \qquad (1)$$

where T_s = stagnation temperature

         T_a = ambient atmospheric temperature

         γ = specific heat ratio

         M   = Mach number

3
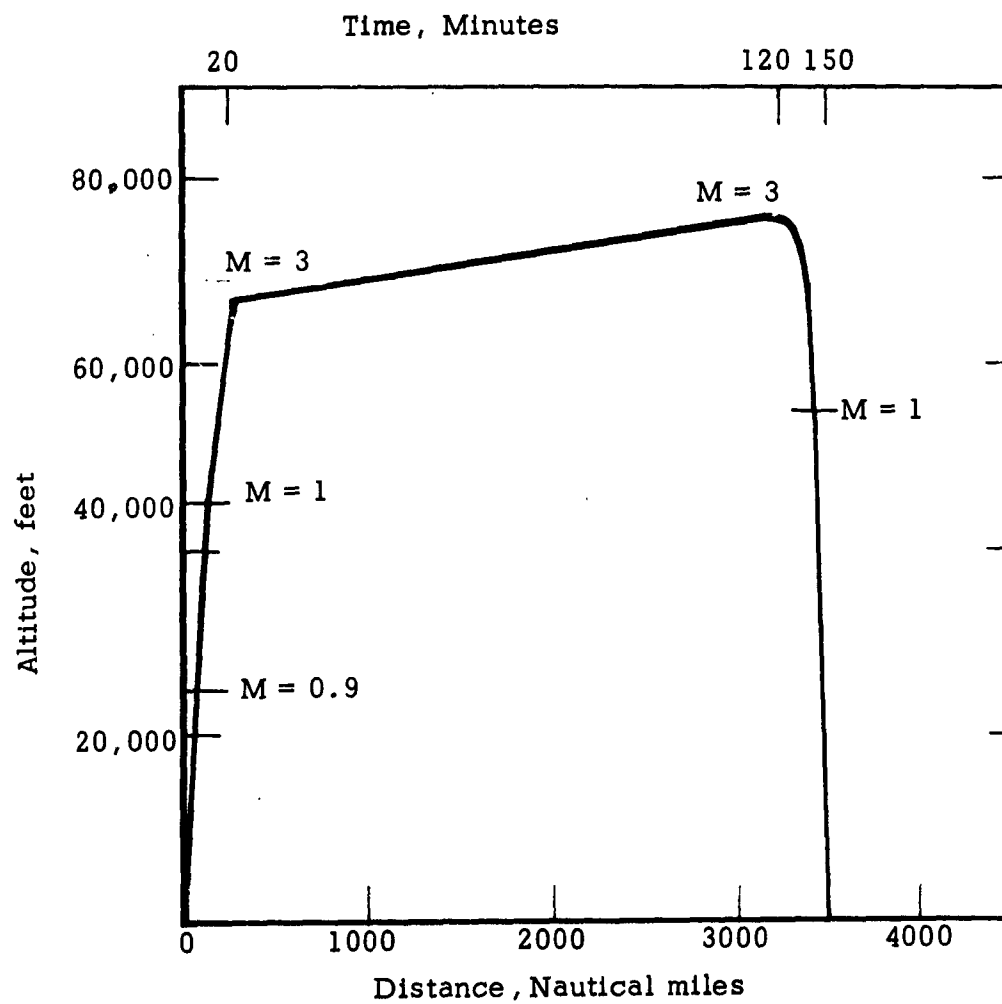
Figure 1. Typical Flight Plan

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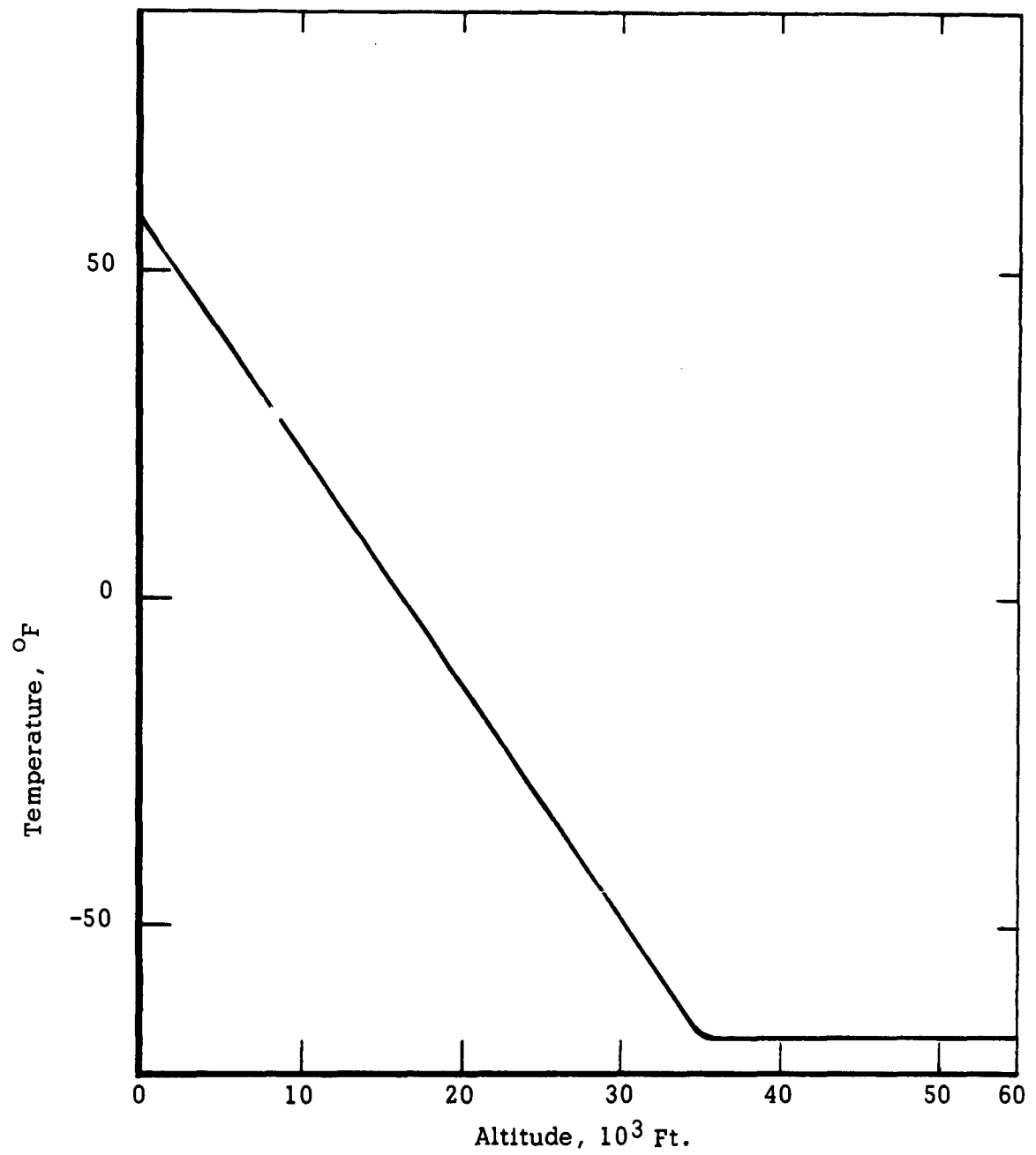
Figure 2. Variation of Temperature with Altitude

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Typical values for stagnation temperature are listed in Table 1.

Table 1. Stagnation Temperatures for Various Conditions

$$\gamma = 1.4$$

Altitude	T_a	Mach Number		
feet	$^\circ F$	1	2	3
Sea Level	60	163	475	993
20,000	-12	78	346	794
Above 40,000	-69	9	243	633

The variation of specific heat ratio, γ, with temperature and composition has not been included in the calculation. The variation of γ with temperature is illustrated in Figure 3 (data of Ref 5).

In order to illustrate the significance of these temperatures in terms of the maximum temperatures which could result for typical flight plans, temperature versus Mach number curves have been plotted for various altitudes in Figure 4. The dashed line is a rough plot of the flight plan shown in Figure 1. The solid line for 40,000-80,000 feet represents the continuation of the flight plan. It is significant that excessively high temperatures are not encountered during the initial acceleration and climb phases of the flight which lasts for approximately 20 minutes.

The maximum temperatures likely to be encountered are, from this point in the flight plan, a function of the maximum Mach number. This temperature varies from about 320°F at a Mach number of 2.2 to about 640° at a Mach number of 3.0, each temperature based on an ambient temperature of -69°F above 40,000 feet.

c. Aircraft Skin Temperature

The stagnation temperatures discussed in the previous section indicate maximum temperatures resulting when the air comes to zero velocity and no thermal losses have occurred. Such temperature levels are realistic for leading edges of various portions of the aircraft, so-called stagnation points. At other positions, however, the surface temperatures will be less than the maximum stagnation temperature. One may indicate such temperatures in terms of a fraction of the maximum stagnation temperature as follows:

$$T = \eta_c T_s \qquad (2)$$

6
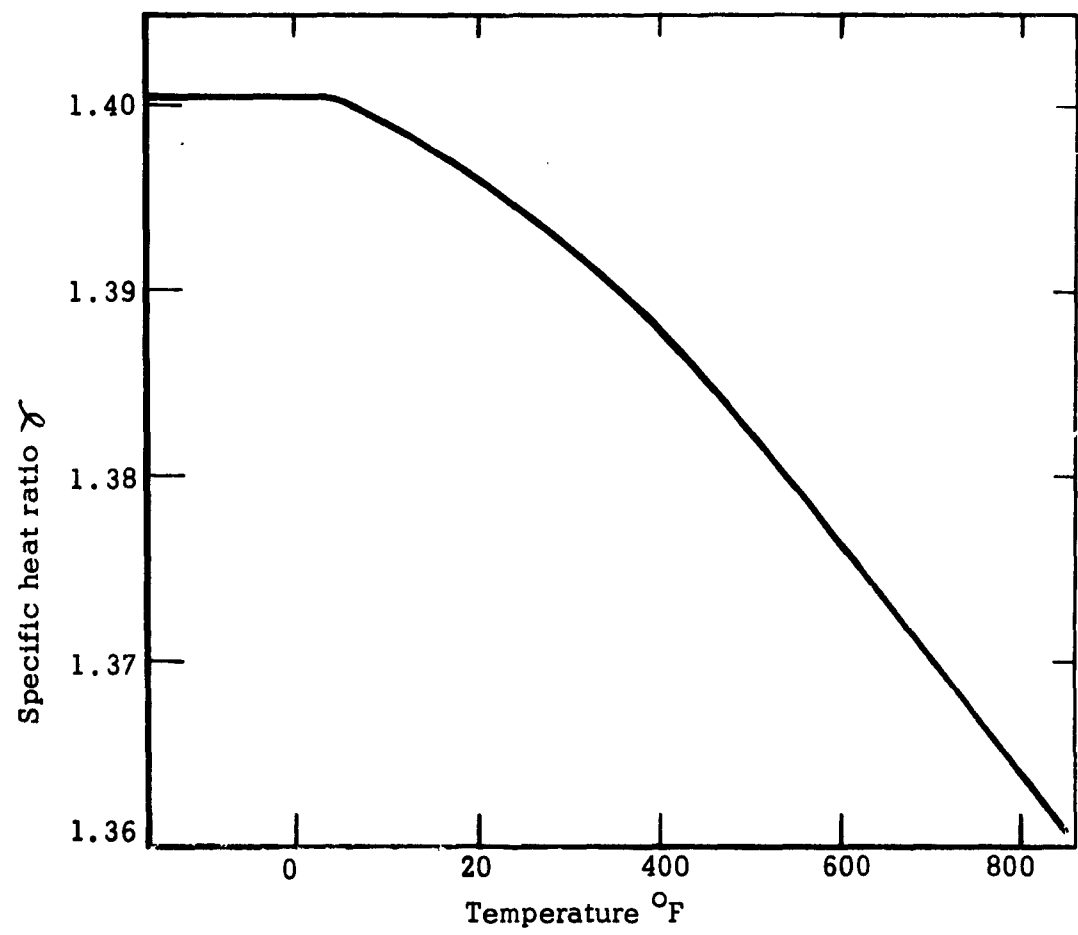
Figure 3. Variation of γ with Temperature

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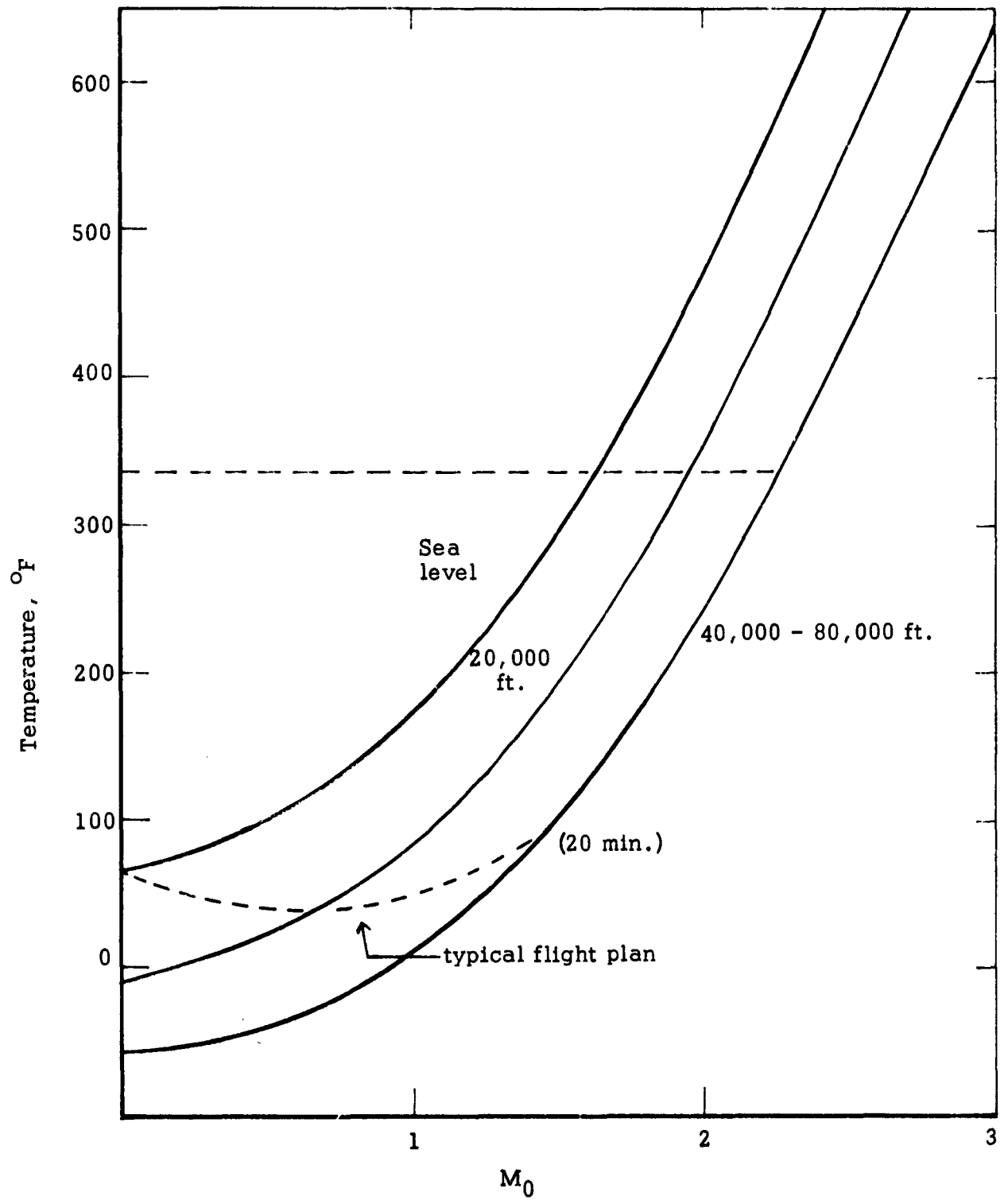
Figure 4. Maximum Stagnation Temperatures

where T = temperature of gas near surface

T_s = stagnation temperature

η_c = correction factor

The use of the more conventional term, recovery factor which would appear in equation (1) in the form (Ref 4)

$$\frac{T_R}{T_a} = 1 + R\left(\frac{\gamma - 1}{2}\right) M^2 \qquad (3)$$

where T_R = recovery temperature

R = recovery factor

has been avoided since the recovery factor is a more precisely defined quantity than the empirical correction factor η_c in equation (2). A more reasonable form for introducing the correction factor might be:

$$\frac{T}{T_a} = 1 + \eta_R \left(\frac{\gamma - 1}{2}\right) M^2 \qquad (4)$$

which, at least, preserves the form of equation (3).

A major portion of the effects producing lower than stagnation temperature is the fact that the air does not come to rest near the surface but is still flowing with a velocity greater than zero. Other factors which influence the actual level of temperature near the surface are heat transfer to the free stream and through the surface itself.

The result of having a correction factor less than one is that a substantial portion of the air near the external surfaces of the aircraft, and hence the temperature of these surfaces is below the maximum stagnation temperature. Some indication of the possible surface temperature likely to occur for a Mach 3 aircraft is illustrated in Figure 5 (Ref 2). This figure indicates surface temperatures between 450°F and 600°F for a Mach 3 aircraft. A crude estimate for other supersonic flight Mach numbers can be made by multiplying the numbers shown on the figure by the ratio of the stagnation temperature at that Mach number to the stagnation temperature at Mach 3. This method relating the temperatures of Figure 5 to other flight Mach numbers is equivalent to assuming that the correction factor is independent of Mach number, which is not strictly true.

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Temperature, ^{O}F

600
600
530
500
460
470
450
440
480
470
600
600
1200
450
600

Dashes indicate fuel storage
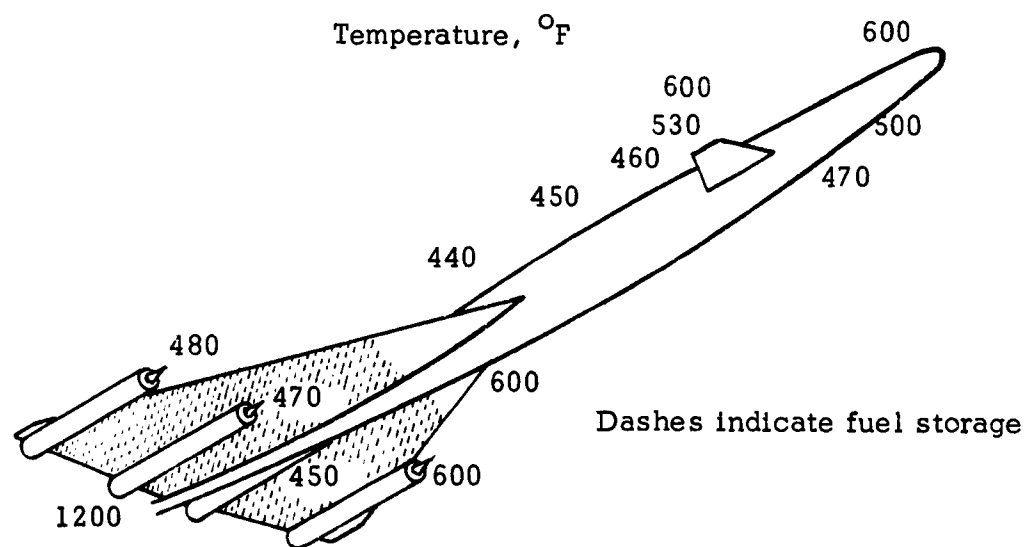
Figure 5. Typical Temperature Pattern and
Fuel Storage Area

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The 1200°F temperature shown on the figure is the engine exhaust gas temperature and presumably would be independent of flight Mach number.

An important aspect of the fire hazard problem involves the temperatures which could be encountered as a result of damage to the aircraft structure. In some ways the possible damaged configurations may be more critical since the causes of the damage may have also produced damage to fuel, oil, hydraulic fluid, or other flammable fluid systems. The likely temperatures to be encountered in a damaged configuration are difficult to estimate. Some estimates can be made, however, of likely changes in the temperature environment due to change.

The result of a small opening in the aircraft skin would be contact between the boundary layer air and the air contained in a bay. In those locations where the local pressure exceeds the pressure inside the bay, boundary layer air would flow into the bay. If the bay is essentially sealed, the air coming to rest within the bay would tend to increase in temperature. For modest flows, it is likely that the heat capacity of the bay would be sufficiently large compared to that of the air that an appreciable temperature rise would not occur.

The effect of a large opening due to damage is also difficult to predict since the location and nature of the damage plays an important role in the temperature which will result. It must certainly be expected, however, that for some cases full stagnation temperature can be reached. The only conservative assumption for large holes in leading edges of various structural members is that stagnation temperature will be reached. In the case of such damage, a configuration of the form

Shock wave

Flow
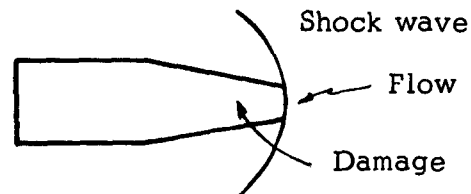
Damage

may be visualized. Although such a configuration represents a poor diffuser, total temperature is generally conserved and it can be expected that temperatures close to stagnation temperature will be achieved.

Quite likely such damage to a leading edge will result in a configuration of the form

Bow shock

Flow
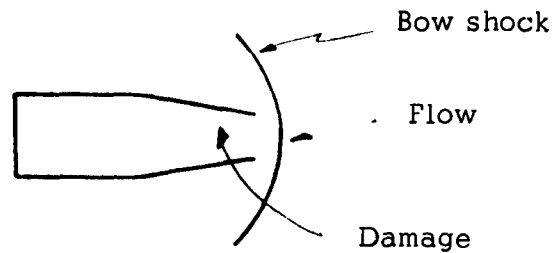
Damage

Here, too, one must expect that near-stagnation temperature will result.
While the use of stagnation temperature under such damage conditions is
conservative, the actual temperature tending to be somewhat lower, this
is certainly the proper estimate for a fire hazard evaluation.

The situation is somewhat more complicated if the damage occurs
along a surface parallel to or nearly parallel to the flow. It has already
been indicated that a small opening will probably n . change the tempera-
ture environment. A large opening, however, wi'' . ter local temperatures.
Consider the following situation.
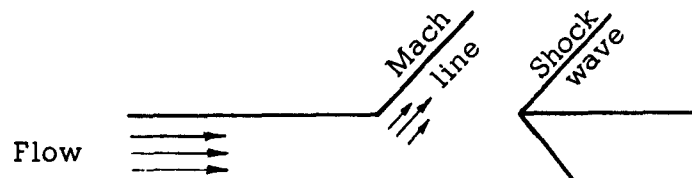
Flow

The flow will expand around the leading edge of the opening and tend
to assume a direction parallel to the Mach line whose angle is given by:

$$\propto = \arcsin \left(\frac{1}{M} \right) \tag{5}$$

where $\propto$ = Mach angle

M   = Mach number

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Although an analysis of the temperature rise is complicated by the three-dimensional flow and complex geometry of the damaged area, the general characteristics of the temperature pattern will include a slightly decreased temperature near the expansion and an increased temperature where the flow comes to rest or impinges on the trailing edge of the damage where a shock wave will undoubtedly result. If the damage involves the external skin of a closed bay, the effects described will be of a transient nature, the final state involving an increase in the temperature from the initial condition to a value near to but slightly below stagnation temperature. Here again, the possibility of achieving stagnation temperature is sufficiently great that this represents the only conservative estimate for a hazard analysis.

A similar conclusion results if the damage consists of a protuberance in the surface as illustrated below:

Flow ⟶   Bump

Assuming that the height of the bump exceeds the boundary layer, the presence of the bump will produce a compression wave with a resulting increase in temperature. The result is a local hot spot with temperatures again approaching stagnation temperature.

In general, then, it may be assumed that damage to the external skin of the aircraft will result in a local increase in temperature. The exact level of temperature achieved is strongly dependent on the nature of the damage. A calculation of the exact temperature increase for specific damage configurations is outside the scope of the present study. From the point of view of an analysis of fire hazards it must be assumed that the increase in temperature in certain areas will cause the local temperature to approach stagnation temperature. The increase in temperature resulting from even minor damage represents one of the important differences between supersonic and subsonic aircraft.

d. Fuel and Fuel Tank Temperatures

Estimates of the fuel and unwetted fuel tank temperature have been made for both the wing tanks, where such tanks are used, and the main fuselage tank. These have been reported in Ref 6. The results are summarized here since these temperatures are a critical factor in the evaluation of fire hazards.

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In some versions of the supersonic transport, it is anticipated that wing tanks will be used to contain the principal fuel required during take-off and acceleration. Except for a residual fuel content these tanks will be emptied during the first 20 minutes of flight. Typical variations of fuel and unwetted fuel tank temperatures for the flight plan illustrated in Figure 1 are shown in Figure 6. Inasmuch as the major quantity of fuel in such tanks will be consumed early in the flight plan, the fuel and fuel tank temperatures are essentially the same as shown in Figure 4, the temperature level being of the order of 75°F. Toward the end of the 20 minute acceleration and climb period, the temperature environment of the aircraft assumes higher temperature levels. The residual fuel shown by a dotted line, will increase in temperature.

The increase in temperature of the residual fuel will depend, in part, on the volatility of the fuel and the rate of vaporization of the fuel, as well as on its quantity and heat capacity. As the tank temperature rises, the fuel temperature will lag behind but will increase in temperature. At temperature levels at which the fuel has appreciable vapor pressure, the fuel will boil tending to restrict its temperature rise. The temperature rise to a condition where appreciable vaporization occurs will depend on the rate of heat input to the liquid fuel and the heat capacity of the fuel. Once vaporization of the fuel begins, the temperature rise of the residual fuel will depend on the volatility of the fuel and the pressure within the tank.

If the fuel vaporizes completely, the condition of such an "empty" tank will be fuel vapor at a temperature equal to the unwetted tank wall temperature. If the fuel contains high boiling residues then the condition of such an "empty" tank will consist of a liquid residue and vapor, all at the temperature of the tank walls. The temperature history of the fuel in an essentially empty tank will lag behind but will closely follow the temperature of the tank itself.

The unwetted tank wall is shown to experience a rapid rise in temperature during the period 20 to 50 minutes after take-off. The estimated maximum wall temperature is of the order of 500°F for a Mach 3 aircraft. It is to be noted that the 500°F temperature is of the same order of magnitude as the aircraft skin temperature shown in Figure 5 for likely fuel storage areas indicated in Figure 5. It is certainly a reasonable assumption that the unwetted fuel tank walls will come into equilibrium with the adjacent aircraft structure unless protective insulation is used.

A typical temperature history for the fuel and unwetted fuel tank wall for a fuselage tank is shown in Figure 7. The tank wall profile is the same as that shown in Figure 6 for a wing tank. The fuel temperature will continue to rise during the course of the flight reaching temperatures of the order of 225°F. The temperature rise is limited by the heat capacity of the fuel in a tank containing appreciable fuel during the entire flight. For this reason the fuel temperature in the main tanks does not show the possibility of a continuously rising temperature approaching the tank wall temperature.

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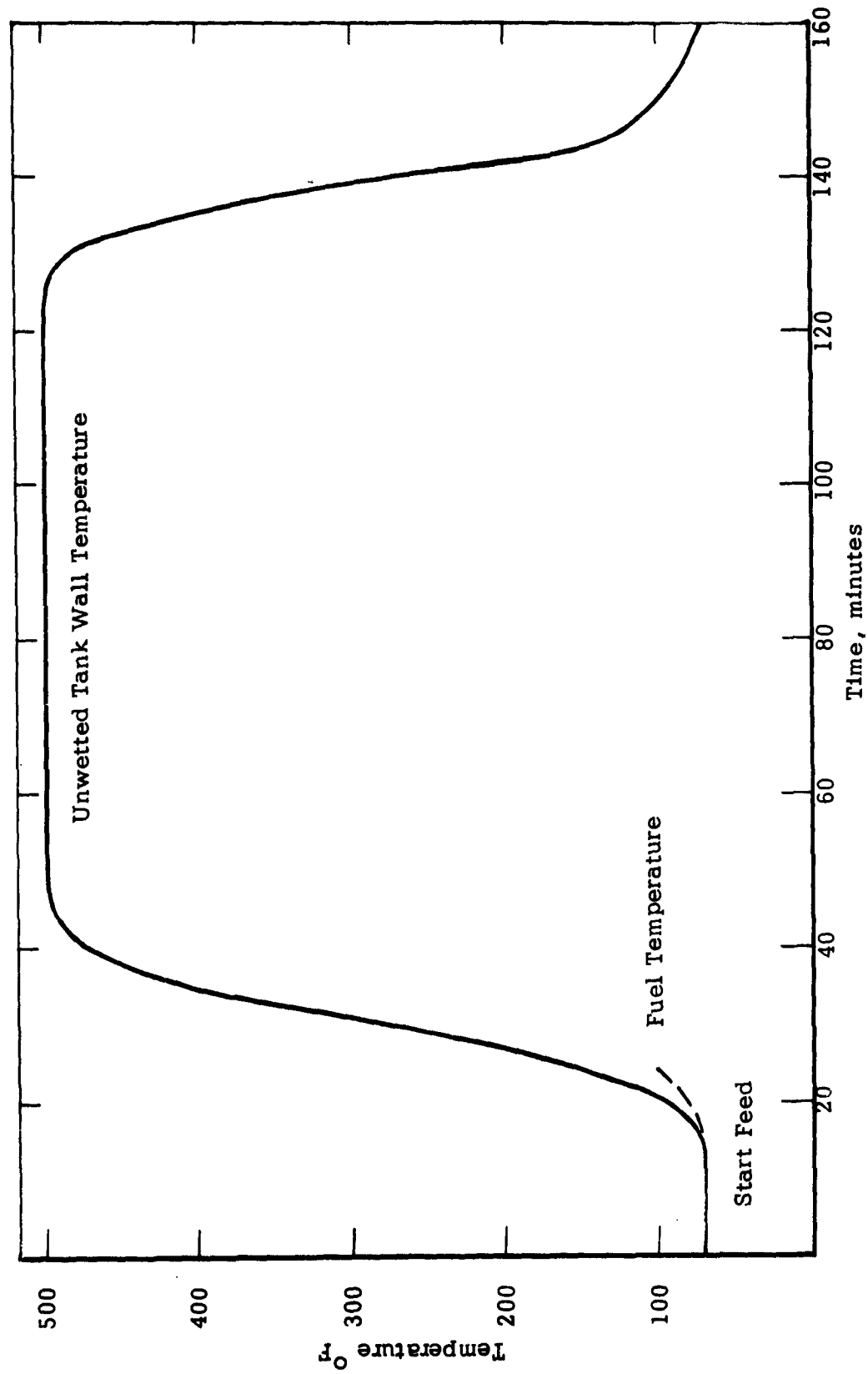
Figure 6. Wing Tank- Fuel and Tank Temperature

15
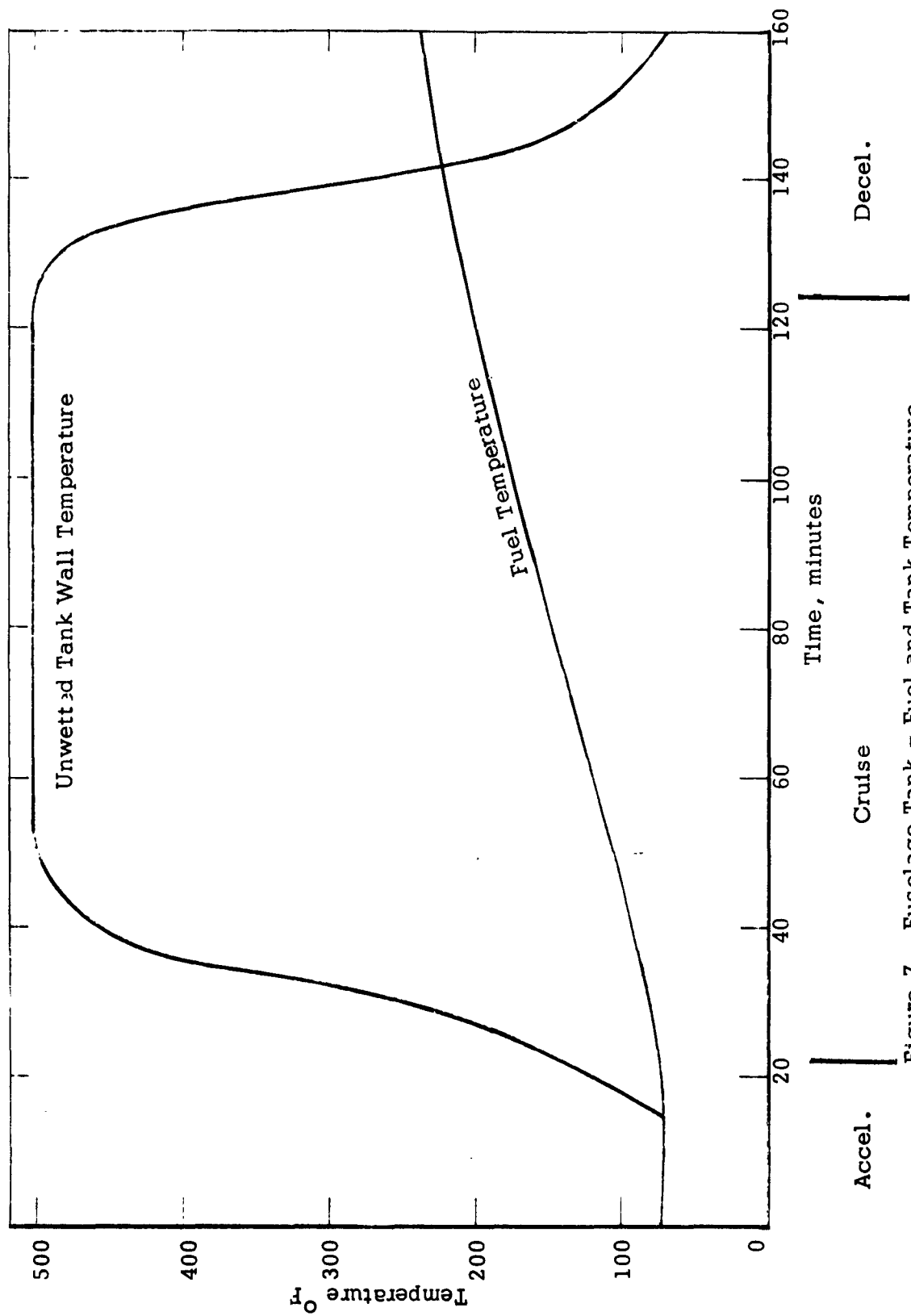
Figure 7. Fuselage Tank – Fuel and Tank Temperature

There are regions within the aircraft where the fuel temperature rises to higher levels. Heat added to the fuel by pumping and additional heat added during passage of the fuel through the hot area near the engine raise the fuel temperature during flow as contrasted with its storage temperature. An estimate of likely fuel temperatures under such conditions was reported in Ref 6 and is presented in Figure 8.

In the situation of a damage configuration, as with the other portions of the aircraft, one would expect an increase in the temperature of the fuel tank wall. We assume here no actual damage to the tank itself but only to the compartment containing the tank. If the damage is of such a nature that a major flow of air does not occur, one would expect that the fuel temperature would not be greatly affected. If the damage is of such a nature that a rapid flow (subsonic) occurs over the fuel tank, then the fuel should increase in temperature but relatively slowly compared to the tank wall. The fuel acts as a relatively efficient heat sink. Vaporization of the fuel tends to maintain a constant temperature. In the case of a fuel composed of a mixture of many hydrocarbons, the boiling point of the fuel increases as the more volatile components evaporate. The result is an increase in the bulk temperature of the fuel. The rate of vaporization is governed chiefly by the rate of heat transfer to the fuel. The temperature change in the fuel can be obtained from an ASTM distillation curve which relates the fuel temperature with the quantity of material evaporated. Interpretation of ASTM distillation data is discussed in the section dealing with fuels.

3.   Pressure

The ambient pressure to which the aircraft is exposed will, of course, depend upon the flight altitude. A plot of ambient pressure versus altitude is given in Figure 9. The most important feature of the figure is the low ambient pressure level during most of the flight.

The actual pressure distribution over the aircraft surface will, of course, differ from the ambient pressure, higher levels of pressure existing on lifting surfaces and lower levels of pressure on opposite surfaces. These differences will be of second order importance from the point of view of fire hazard so that it is reasonable to assume that most interior portions of the aircraft, not deliberately pressurized, will be at the local static pressure of the aircraft skin with which they communicate and that this pressure corresponds to the static pressure at flight altitude.

There is associated with pressure the same type of consideration which relates static temperature to stagnation temperature. The stagnation pressure represents the maximum pressure which the aircraft could experience. The maximum stagnation pressure can be calculated from the relationship:

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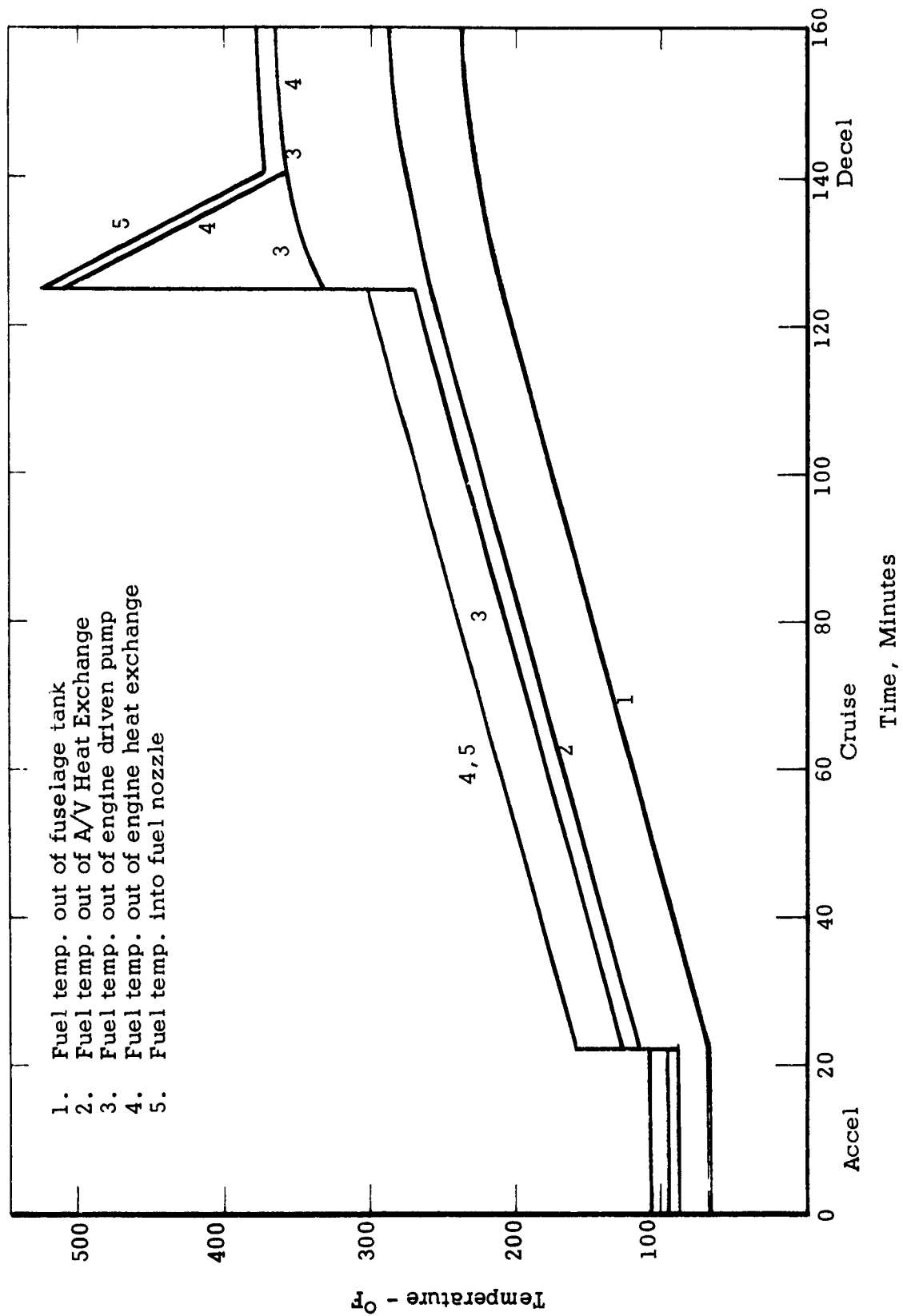
Figure 8. Supersonic Transport Fuel Temperatures

Legend:

1. Fuel temp. out of fuselage tank
2. Fuel temp. out of A/V Heat Exchange
3. Fuel temp. out of engine driven pump
4. Fuel temp. out of engine heat exchange
5. Fuel temp. into fuel nozzle

X-axis: Time, Minutes (Accel, Cruise, Decel)
Y-axis: Temperature - °F
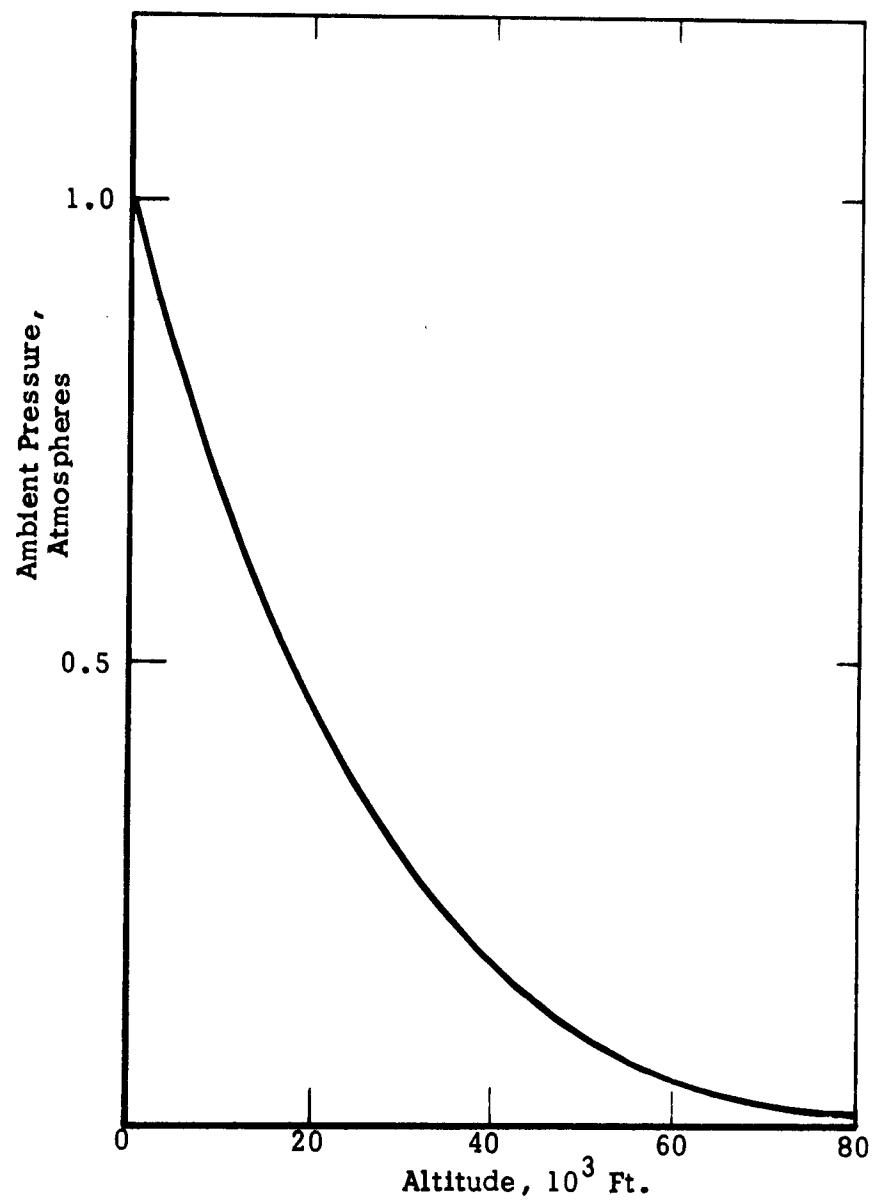
Figure 9. Variation of Pressure with Altitude

$$\frac{P_s}{P_a} = \left(1 + \frac{\gamma - 1}{2} M^2\right)^{\frac{\gamma}{\gamma - 1}} \qquad (6)$$

where P_s = stagnation pressure

               P_a = ambient static pressure

               γ = specific heat ratio

               M = Mach number

      Typical values for stagnation pressure at various altitudes and Mach numbers are listed in Table 2.

Table 2. Stagnation Pressures for Various Conditions

$$\gamma = 1.4$$

Altitude	P_a	Mach Number		
Feet	atm.	1	2	3
Sea Level	1.00	1.89	7.82	36.7
20,000	.46	.87	3.58	16.9
40,000	.18	.34	1.40	6.6
60,000	.07	.13	.54	2.6
80,000	.03	.06	.38	1.1

      The variation of specific heat ratio with altitude has not been included in the calculation.

      In order to illustrate the significance of these pressures in terms of the maximum pressures which could be encountered for the typical flight plan, pressure versus Mach number curves for various altitudes have been plotted in Figure 10. The dashed line indicates roughly the maximum stagnation pressure associated with the acceleration and climb portion of the flight plan shown in Figure 1.
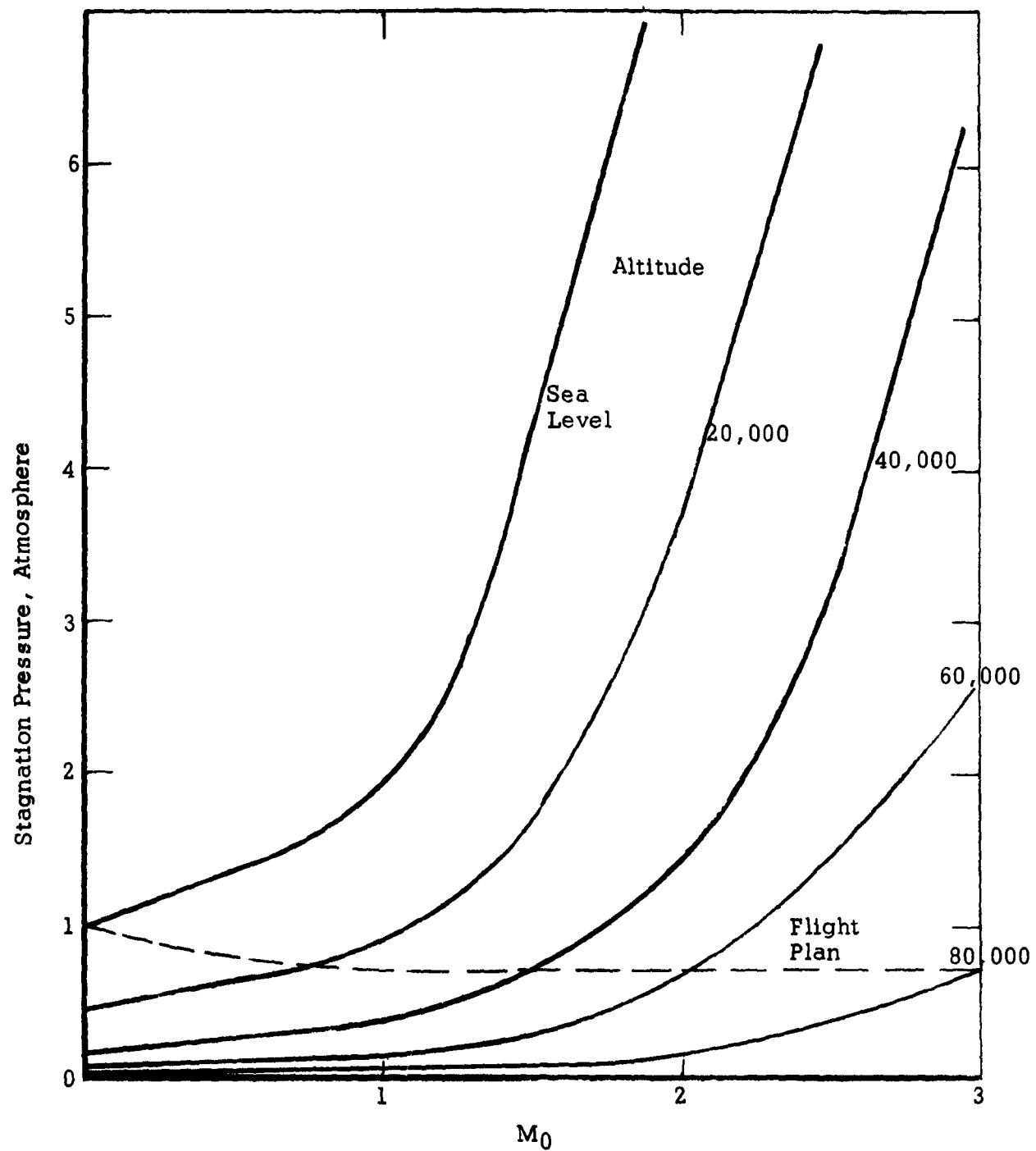
Figure 10. Stagnation Pressure versus Mach Number

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The complete range of pressures which should be considered during the flight plan can be represented by the ambient pressure at each altitude given by the Mach number zero points to the maximum stagnation pressures associated with each altitude and pressure. During most of the flight plan the maximum stagnation pressure is of the order of sea level static pressure or lower. The maximum stagnation pressure occurs at the end of the climb portion of the flight plan. Although the descent portion of the flight plan is not shown in Figure 10, the rapid deceleration to Mach 1 illustrated in Figure 1 indicates that maximum stagnation pressures will be below those of the acceleration and climb phase of the flight.

Despite the high stagnation pressures associated with Mach 3 flight, the pressure levels over most of the aircraft surface will be the ambient altitude pressure. In the vicinity of shock attachment and reflection points, however, the pressures will be considerably higher approaching stagnation pressure at stagnation points. A typical pressure profile for the system illustrated below

shock wave

would be

P
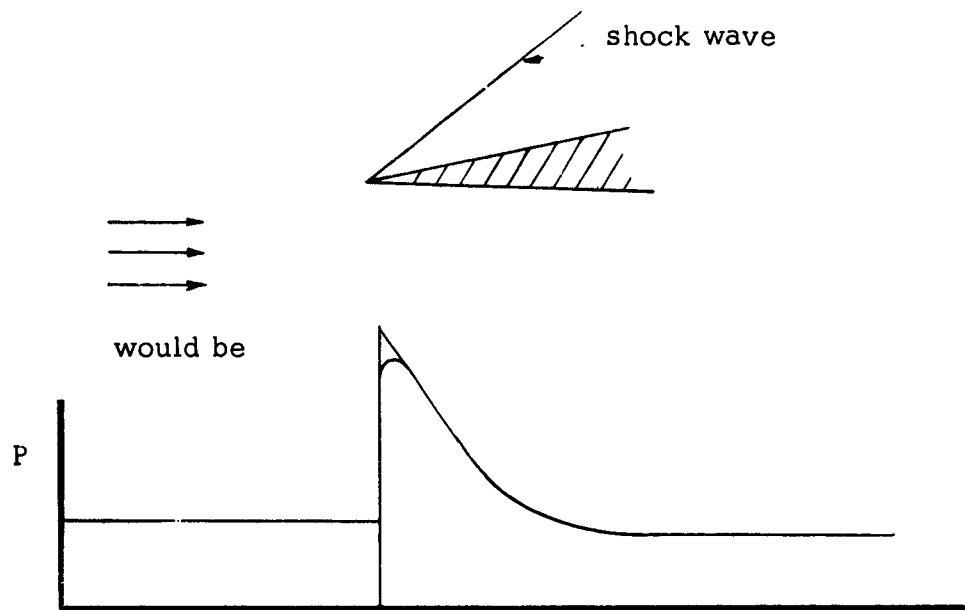
Similar pressure peaks will be associated with points of shock wave reflection in those configurations where shock interaction effects are used to provide lift forces. The exact location of such points of high pressure will depend on the particular aircraft design. These high pressure points will exist on the external skin of the aircraft and, under normal conditions, would not be transmitted to interior regions.

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Some bays within the aircraft will be pressurized during flight. The cabin will, of course, be maintained at an equivalent altitude of 3000 to 5000 feet. The baggage compartment may also be pressurized but probably not to the same extent used in the cabin. The fuel tanks may be pressurized or partially pressurized. Consideration has been given to the possibility of pressurizing the fuel tanks to minimize losses due to evaporation. While the exact levels of pressure within the fuel tanks will vary for different aircraft designs, the use of pressurizing systems to maintain tank pressures of the order of 3-5 psia (Ref 6) have been considered.

The effect of damage to the aircraft, in general, will result in higher local pressures in the damaged location. Usually the effects of damage on pressure will follow the same trends as those presented earlier for temperature. Several typical damage configurations will be discussed in terms of simplified geometries.

Consider a damage situation which produces a bump in the outer skin of the aircraft. If the protuberance extends beyond the boundary layer, a shock wave will result producing a local increase in pressure and temperature. For the case of a turbulent boundary layer, and approximating the bump as a step, the following situation would result (Ref 7).
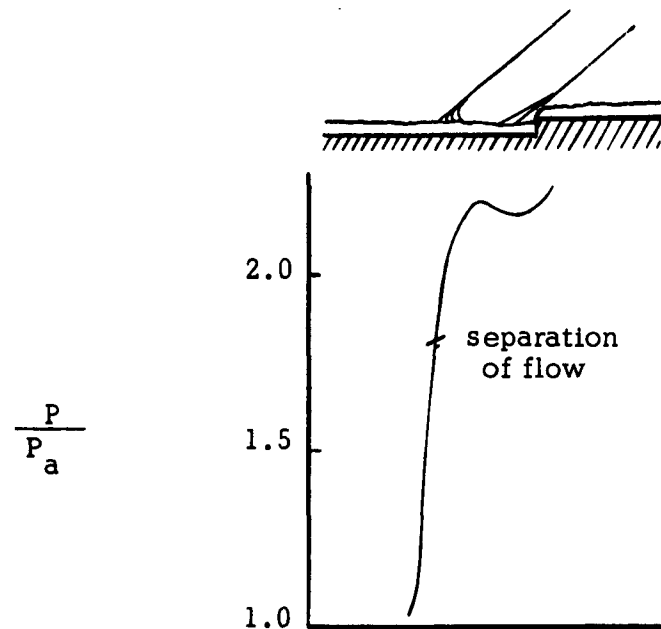
The data are shown for a Mach number of 2.3. P/P_a can be calculated for other Mach numbers in the range $1.5 < M < 3.5$ by the equation (Ref 8)

$$\frac{P}{P_a} = \frac{\gamma}{2} M^2 \left[\frac{3.2}{8 + (M-1)^2} \right] + 1 \qquad (7)$$

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A dent in the surface, represented by a reverse step
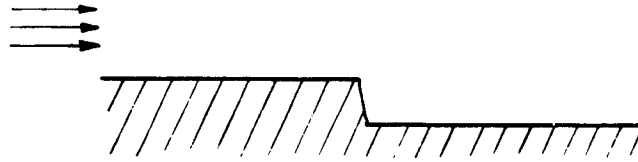
results in a local decrease in pressure as a consequence of the expansion around the corner.

A cavity or hole in the surface can be approximated roughly by a combination of the forward and reverse steps. The general behavior in such a cavity involves an expansion at the leading edge producing a lower pressure and a compression at the trailing edge resulting in a shock wave and an elevated pressure. The exact behavior is a function of the size of the cavity.

The pressure profiles for typical cavities are shown below:
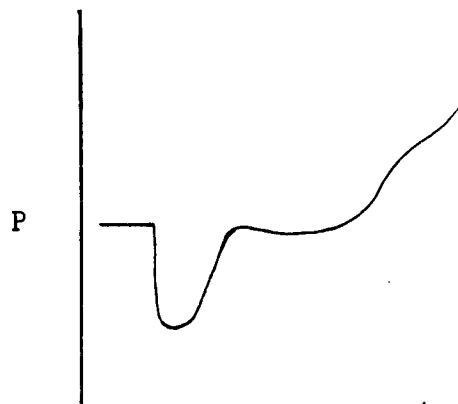
Long Cavity   Short Cavity

24
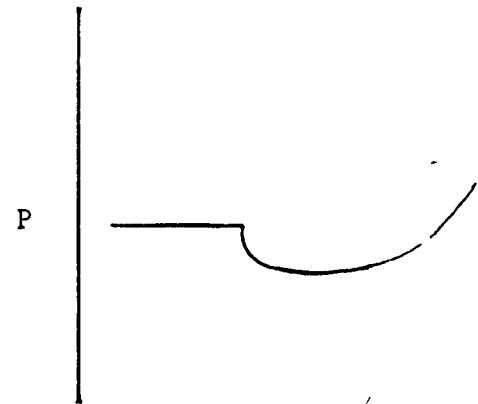
Illustrated for both cases is an initial decrease in pressure followed by an increase in pressure due to the shock wave. The pressure changes are larger for a long cavity than for a short cavity, a short cavity consisting of one in which the boundary layer bridges the gap rather than dipping down into it (Ref 9).

In some cases a resonant condition can result in which the pressure and temperature oscillate within the cavity. While very high temperatures (above stagnation) can result, the pressure level does not exceed the values for the steady flow case. In general the pressure generated by the situations illustrated is of the order of twice the free stream ambient pressure.

The supersonic transport pressure distribution is also affected by the presence of shock waves intersecting the aircraft from other locations on the aircraft. Such interference shocks are considered, in fact, as a part of the design concept to produce lift. The impingement of a shock wave on a surface will produce a local region of high pressure and temperature. In a simplified form the situation illustrated below describes a typical impingement for a region of turbulent boundary layer:
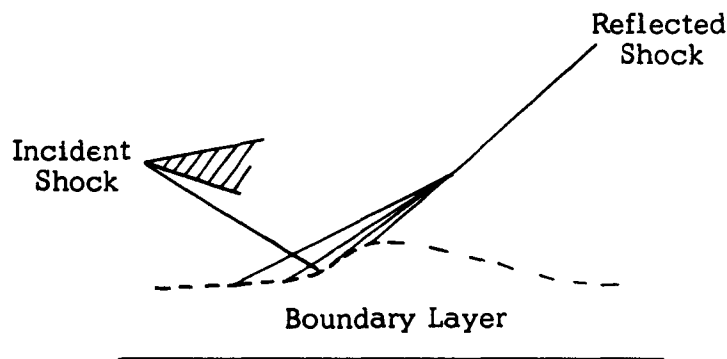
An indication of the pressure rise which can exist at the point of impingement for different free stream Mach numbers and boundary layer Reynolds numbers is given in Figure 11 (Ref 7). The variable P_S represents the pressure at the point of separation which approximates the point of impingement. The ratio to ambient static pressure can be obtained from the relationship:
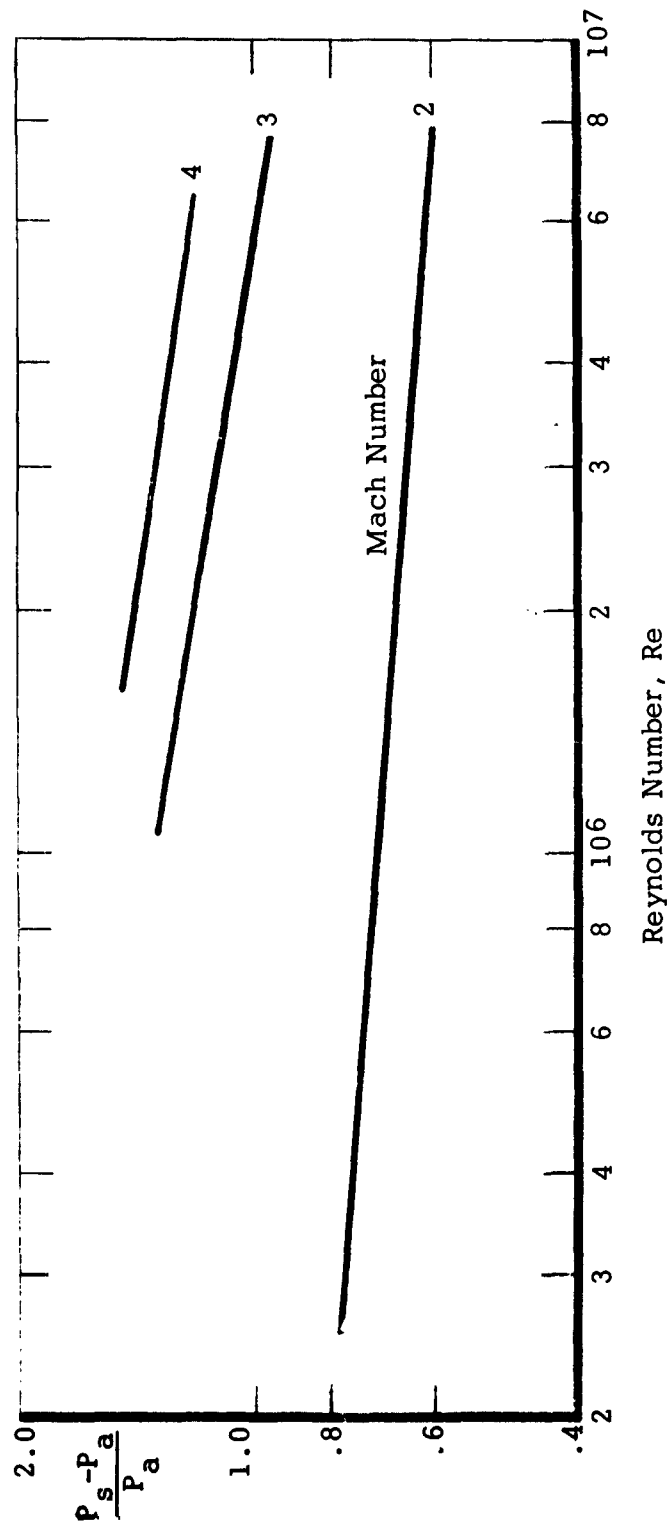
Figure 11. Pressures of Impinging Shock

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$$\left(\frac{P_s - P_a}{P_a} \right) + 1 = \frac{P_s}{P_a} \tag{8}$$

For a flight Mach number of 3, the pressure ratio varies from about 2 to 3 depending upon the Reynolds number.

Examples have been presented for typical configurations which could lead to pressures greater than the ambient altitude pressure. A detailed analysis of the flow is beyond the scope of this report and, in fact, would require state-of-the-art advances in the calculation of supersonic flow characteristics for complex geometries and shock interactions. A general statement concerning pressures under damage conditions, consistent with much of the data in existence is that pressures of the order of 2-3 times ambient appear reasonable for most damage situations. Excluded from this generalization would be configurations which contain projections into the flow of sufficient magnitude that stagnation pressure can result. It is unlikely, however, that the aircraft would maintain full cruise speed under such conditions.

4. Ventilation

The problem of ventilation or air flow rates in various bays within the aircraft consists of essentially two different areas of concern. The first of these is the normal "breathing" of the bay as it adjusts to the local ambient pressures with which it is in contact. The fuel tanks represent the major volume within the aircraft in which breathing is a primary variable. In other bays, particularly those in which flammable fluid leakage may occur, breathing of the bays may play a role in determining local flammable-air ratios and local flow velocities. The second type of ventilation is represented by a major flow of air through a bay either deliberately or as the result of damage.

The normal breathing type of ventilation is the result of the internal volumes of the aircraft attempting to come into equilibrium with its external environment usually as a result of a change in pressure of the external environment, and occasionally as a result of a change in pressure or free volume internally. The latter condition is often encountered in fuel tanks. The flow may be into or out of the bay depending on whether the internal pressure is lower or higher than the external pressure. The quantity of flow will depend on the pressure difference and the free volume of the bay, while the velocity of flow will also depend on the size of the opening through which the flow occurs.

The flow velocity through an opening (or several openings considered as a single opening) can be estimated from the following equation:

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$$U = \left(\frac{V}{A}\right)\left(\frac{1}{P}\right)\left(\frac{dP}{dt}\right) \tag{9}$$

where U = flow velocity

    V = volume of tank or bay

    P = local ambient pressure (assumed equal to tank or vent pressure)

  dP/dt = rate of pressure change with time

    A = area of opening

For an aircraft undergoing a change in altitude, dP/dt can be replaced by

$$\frac{dP}{dt} = \left(dP/dh\right)\left(r/c\right) \tag{10}$$

where dP/dh = change of pressure with altitude

   r/c = rate of climb (a negative value indicates descent)

The mass flow involved in breathing due to altitude change is related to the velocity through the equation:

$$W = \rho AU \tag{11}$$

where W = mass flow per second

   ρ = density = $\dfrac{P\overline{M}}{RT}$

   $\overline{M}$ = mean molecular weight

For a fuel-air mixture the mean molecular weight is given by:

$$\overline{M} = \frac{1 + F/A}{\dfrac{1}{M_A} + \dfrac{F/A}{M_F}} \tag{12}$$

where F/A = mass fuel-air ratio

   M_A = molecular weight of air

   M_F = molecular weight of fuel

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Forced ventilation with cold air will be employed in several areas on the aircraft. The cabin will be air conditioned and the baggage compartment will be cooled. Some of the cooled air may also be used to protect temperature sensitive electronic equipment. The flow velocities in such cooled areas will be low.

Forced ventilation using compressor bleed air or ram air could also be considered for fire protection. It appears unlikely that deliberate forced ventilation will be an important consideration, however, for three reasons: (1) the drag imposed on the aircraft, (2) the likely high temperature, and (3) increased heat transfer due to flowing warm air. While it would appear desirable in some circumstances to use forced ventilation with relatively cold air, such a condition could only be achieved if the Mach number of the air through the desired region remained high. Such a ventilation system, unless carefully designed would impose a large drag penalty. The likelihood of having such open areas seems small, however. Most designs of the supersonic transport show bays jammed with equipment. The deliberate introduction of external air at a high flow rate would result in fairly low velocity flow through a highly blocked path. The result would be the heating of the air close to stagnation temperature. The flow of hot air would increase heat transfer rates above that occurring for quiescent air at the same temperature. Such factors make the use of forced ventilation unattractive.

One source of fairly cool air might be useful for a limited set of circumstances. The rejected cabin air represents a source of cool air which could be used for the ventilation of bays. Such air will probably be useful to cool electronic components but will still be available at temperatures of the order of 200°F for purposes of ventilation. Specific examples of areas within the aircraft where such air may be employed will be discussed in connection with specific hazard problems.

C. FLUID PROPERTIES

The fluid properties, with the exception of thermal stability, to be treated in this section are usually classified as physical properties to differentiate these properties from those which involve chemical reactions. These physical properties include volatility, viscosity, density, etc. Thermal stability, normally a chemical property, has been included in this section for the present report as a matter of convenience. The principal fluid properties not considered here are those associated with combustion, such as ignition, flame velocity, etc. These are treated in a separate section later in the report.

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1.   Fuels

The principal flammable carried by an aircraft is, of course, the fuel.
Several limitations on the nature of the fuel are imposed by the environ-
mental conditions associated with supersonic flight. The high temperature
environment in particular places two severe restrictions on the nature of
the fuel. Low volatility fuels appear necessary to minimize fuel losses
due to boil off or, if pressurized tanks are considered, to minimize the
pressure difference between the tank and its surroundings. The second
requirement is that the fuel must withstand temperatures in excess of
200°F without changes that can affect performance or system reliability.
In this report the discussion of fuels will emphasize low volatility fuels
although, for purposes of comparison and development of correlations, pure
compounds and higher volatility fuels will occasionally be included.

a. Volatility

One of the most important physical properties of the fuel, both from
an operational point of view as well as fire hazard, is the fuel volatility.
It has already been indicated that a low volatility fuel will probably be
chosen for the supersonic transport. A number of different methods of
specifying volatility are used. Each of these, for commercial fuels at
least, apply to different conditions so that an understanding of the methods
is necessary before the data can be used in a hazard evaluation. An
attempt will be made in the succeeding paragraphs to describe the more
widely used methods, their significance and some typical data.

Most fuel specifications include an ASTM distillation curve either in
tabular form or in graphical form. The ASTM distillation consists of an
experiment in which a prescribed initial quantity of fuel is exposed to a
fixed rate of temperature rise. As the temperature increases, fuel boils
away, is collected and its quantity measured. The temperatures at which
10%, 20%, etc. of the fuel have distilled away are recorded and either
tabulated or graphed.

The ASTM distillation curve for a pure substance is quite simple. It
consists of a constant unique temperature which is the boiling temperature
of the fuel. Within very broad limits this temperature is independent of
the quantity of fuel used, rate of heating and other aspects of the experi-
ment which are carefully controlled in an ASTM distillation. For a pure
substance then, the initial point, temperature at which distillate is first
observed, the 10%, 20%....., and the end point, temperature at which the
last distillate is collected would all be the same, the boiling temperature
of the pure substance.

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The situation is more complicated for mixtures and particularly for the complex mixtures which represent commercial fuels. A fairly typical ASTM distillation curve for a commercial turbine fuel is illustrated in Figure 12. The first distillate for this fuel was noted at about 350°F. The 10%, 50%, and 90% points are noted on the figure. The last distillate or end point was noted at about 500°F.

Curves of quite different shape can result depending upon the composition of the fuel. A few typical examples will be discussed. The addition of 5% of a volatile constituent to the fuel of Figure 12 would alter the initial point of the curve, lowering the initial point to a value near to, but not exactly equal to, the boiling point of the volatile component. The 10% point, however, would not be greatly altered and would probably fall near the 5% point in Figure 12. The remainder of the curve would remain almost unchanged.

Another type of distillation curve which is sometimes found, results from a mixture of relatively volatile components with relatively non-volatile components. Such a curve may begin as shown in Figure 12, but if the volatile components are depleted, little additional distillate may be found until a steep rise in temperature has occurred.

The ASTM distillation curve is significant for a number of considerations relative to fire hazards. The quantity of fuel evaporated at each level of temperature can be used to estimate the equilibrium fuel-air composition where the vapor volume of the system is known. The vapor pressure, discussed later in this section, is probably more useful for this purpose, but as will be discussed, the vapor pressure depends on the free volume or ullage for mixtures and therefore depends on the changes in the liquid composition resulting from various degrees of vaporization.

Another use for the ASTM distillation curve is the estimation of liquid fuel temperature as evaporation occurs. Generally the liquid fuel temperature is somewhat higher than the ASTM distillation temperature, but is likely to be of similar magnitude. Consider now the situation which can exist for a fairly small quantity of residual fuel such as might exist in the wing tanks discussed previously. As the environment around the tank increases in level of temperature, the liquid fuel temperature increases. If vaporization can occur, as would be the case for an unpressurized tank, or a tank pressurized to some low value, the temperature of the liquid fuel can continue to increase until the liquid is gone or the liquid fuel temperature and unwetted wall temperature become essentially equal. This situation for a small quantity of residual fuel is contrasted with a large quantity of fuel such as that existing in the main fuselage tanks where the temperature rise is limited by the large heat capacity of the fuel as well as by the large amount of fuel which would have to be vaporized before the liquid temperature could rise appreciably. In the fuel used for Figure 12, for example, the fuel temperature could rise to 500°F before all of the fuel evaporated.

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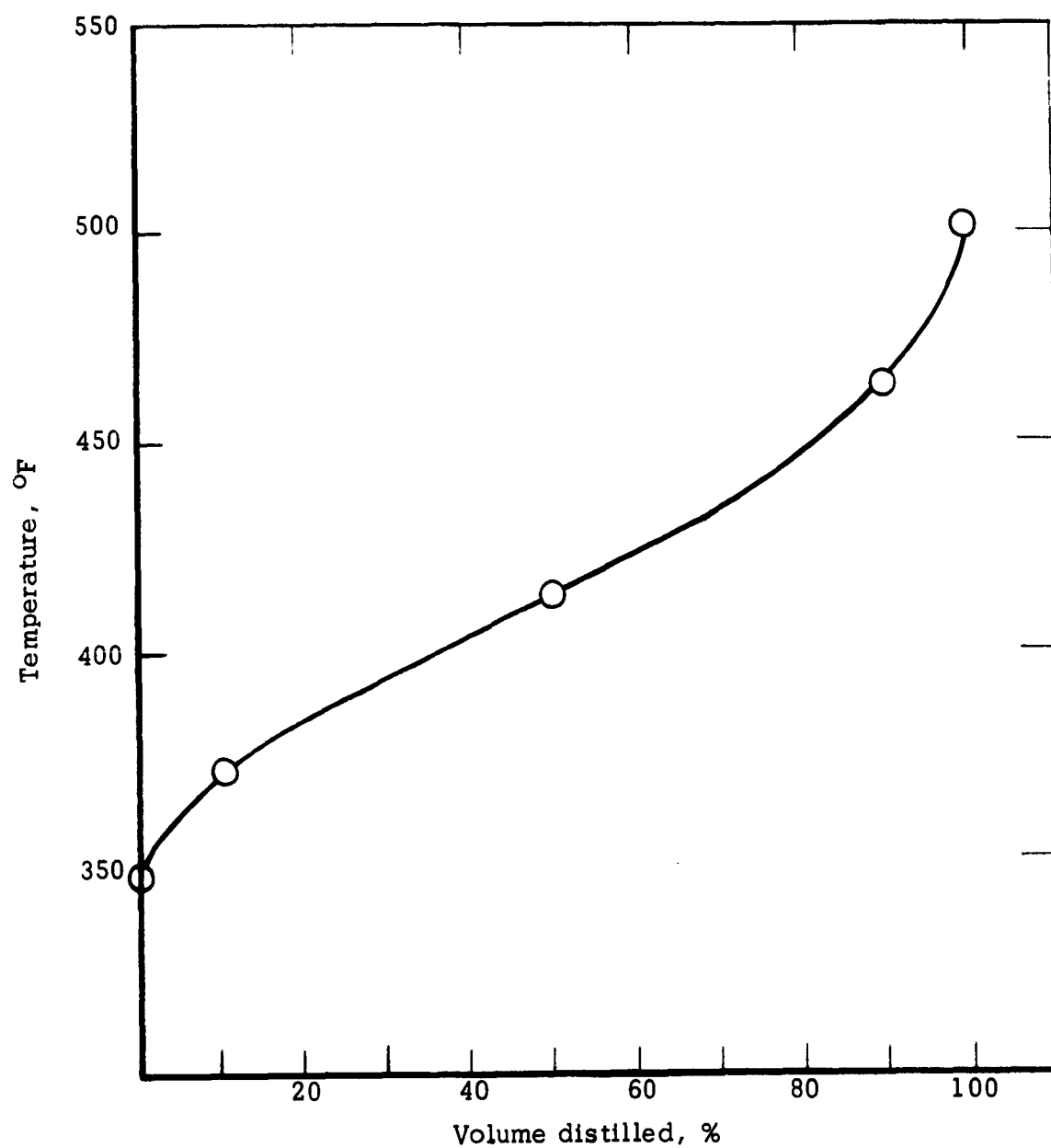
Figure 12. ASTM Distillation of Commercial Turbine Fuel
Normal Boiling Point - 372°F

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Another important criterion of fuel volatility is the vapor pressure. Unfortunately, while the vapor pressure of a pure substance is an unambiguous function of temperature, the vapor pressure of a mixture depends on the quantity of fuel evaporated before an equilibrium pressure is reached at a given temperature. In other words, for mixtures the vapor pressure depends on free vapor volume available or the ullage of the system.

As has been mentioned, the vapor pressure of a pure substance depends only upon temperature. A typical vapor pressure versus temperature curve for n-octane is illustrated in Figure 13. A theoretical relationship between vapor pressure and temperature for a pure substance is the Clausius-Clapeyron equation which is:

$$\log_{10} \frac{P_2}{P_1} = \frac{\Delta \text{Hvap.}}{2.3R} \left(\frac{T_2 - T_1}{T_1 \quad T_2} \right) \tag{13}$$

where   P   = vapor pressure

Δ Hvap.   = latent heat of vaporization

          T   = absolute temperature

          R   = gas constant

This relationship is based on the assumption that the latent heat of vaporization is independent of temperature and that the fuel vapor behaves as an ideal gas. These assumptions are reasonably good for the temperature and pressure intervals of interest in most aircraft hazard studies. The equation suggests that a graph of $\log_{10} P$ versus $^1/T$ should give a straight line. The data of Figure 13 for octane are re-plotted in Figure 14.

In a closed system held at a fixed temperature, the liquid evaporates until an equilibrium condition exists between the liquid and vapor at some specific pressure. For a pure substance, the larger the free volume the more liquid will evaporate, but the final equilibrium pressure will be independent of the free volume. For a mixture, however, the composition of the liquid changes as evaporation occurs due to the preferential evaporation of the more volatile components at the beginning. The change in composition of the liquid depends on the quantity of material evaporated so that the ultimate equilibrium pressure also depends on the quantity of material evaporated.

To overcome the difficulty of changing vapor pressure with the free volume available for evaporation, several different procedures have been followed. One of these procedures involves the definition of a "true" vapor pressure as the equilibrium pressure resulting from evaporation into a very
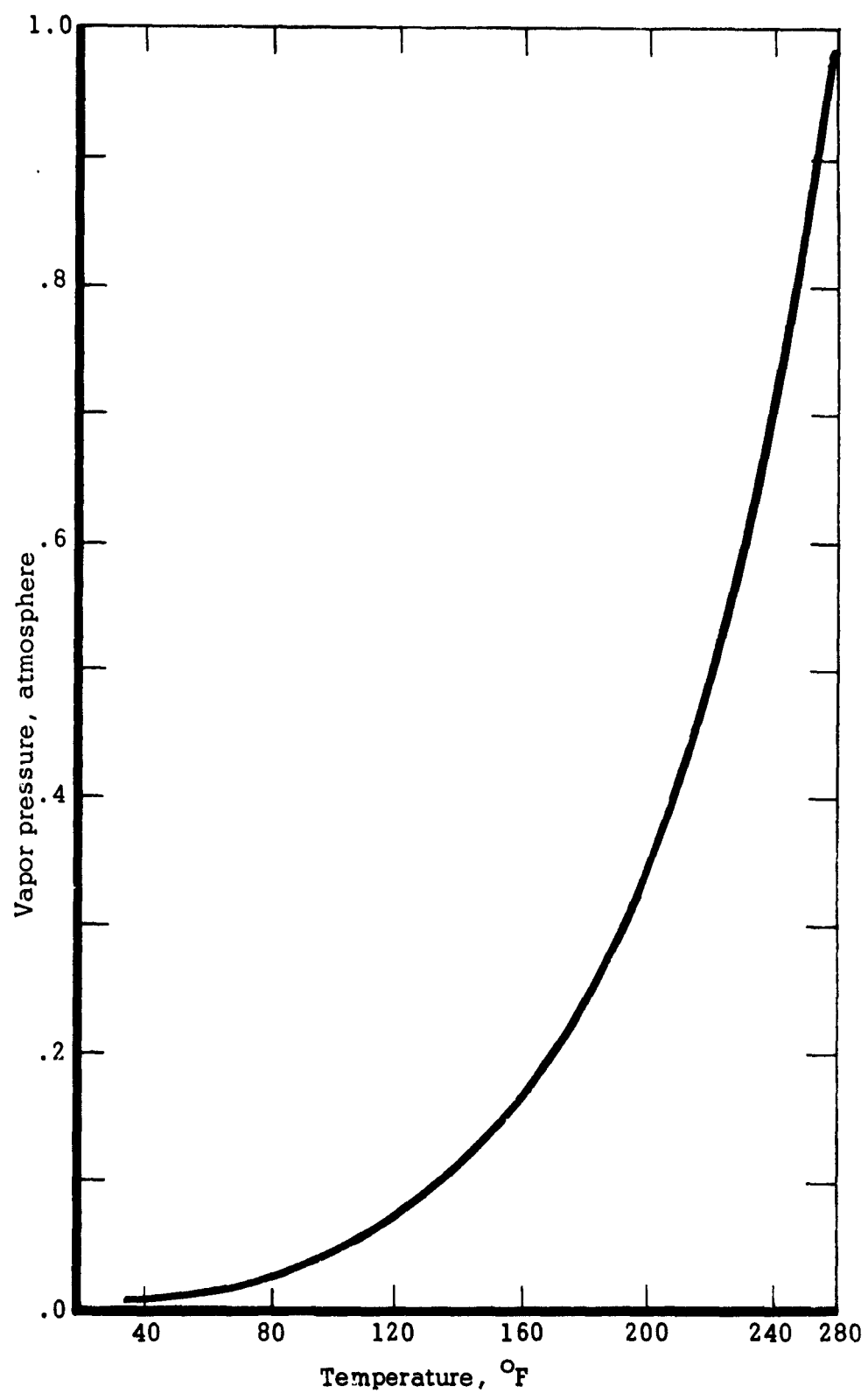
Figure 13. Vapor Pressure of Octane

34
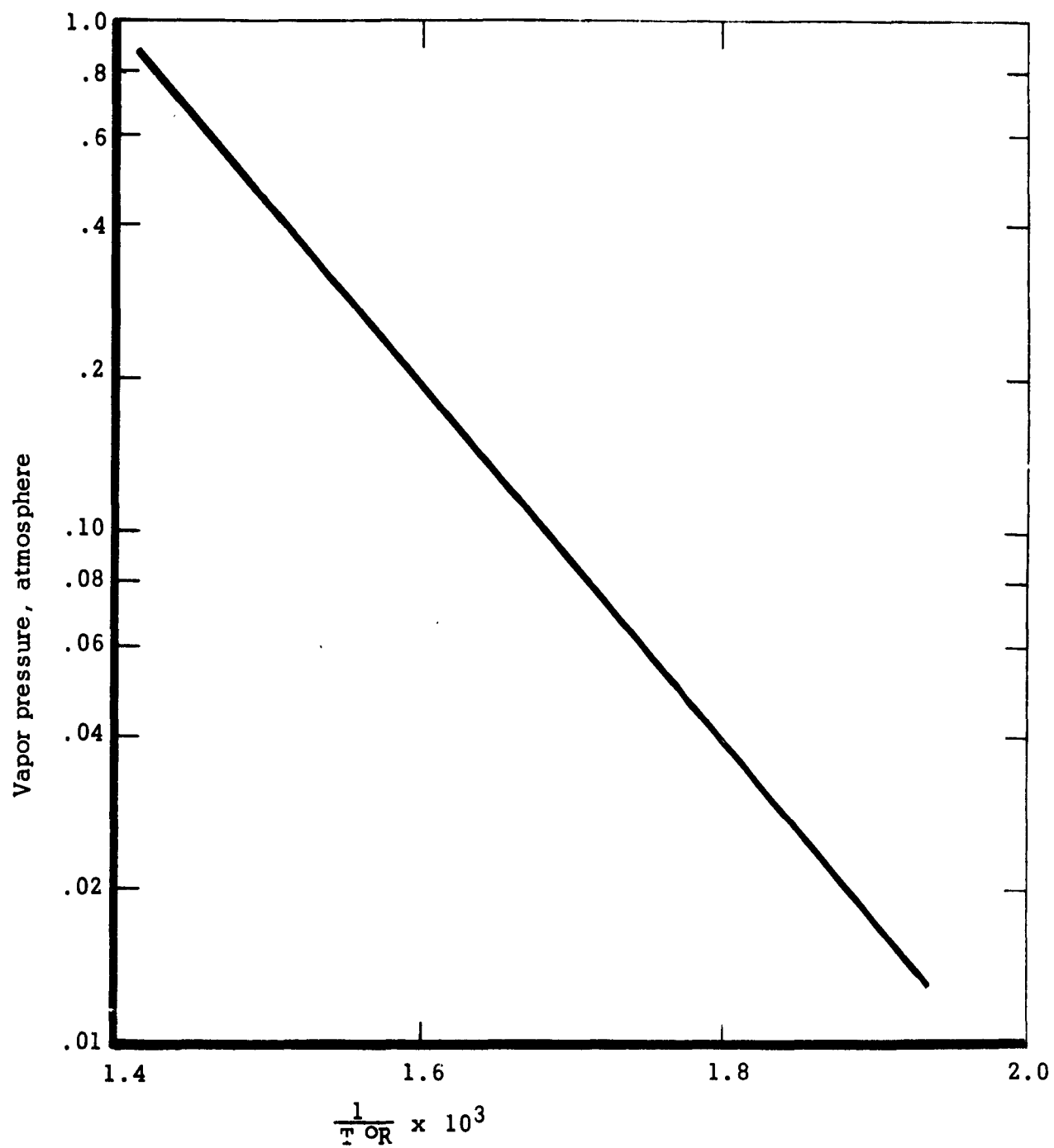
Figure 14. Vapor Pressure of Octane

small free volume or for negligible change in liquid composition. More precisely, the true vapor pressure could be considered as the extrapolation to zero free volume of equilibrium pressures measured at several different free volumes, representing the case for no change in liquid composition. It should be emphasized that such true vapor pressures do not indicate the actual pressure which would be observed in a real situation, particularly if the free volume is large. The only precise way to determine the equilibrium pressure in an actual system is by direct measurement in that system with the exact quantity of liquid fuel used for which the pressure is desired. Decreasing the quantity of liquid fuel has the same effect as increasing the free volume since larger composition changes will be noted as the quantity of liquid decreases.

Some typical "true" vapor pressures of commercial fuels are plotted against temperature in Figure 15.

Another method for obtaining repeatable vapor pressure values is to carefully specify the liquid and vapor volume. Experimenters in different laboratories working with the same fuel will thus measure the same pressure at each temperature. Reid vapor pressure represents one such standardized technique where the liquid and vapor volumes and the temperature for the pressure measurement are carefully specified and controlled. Such standardized techniques, while very useful in comparing similar fuels, give no indication of the pressure for other conditions nor can they be relied upon to give a measure of relative volatility under different conditions. Since the ASTM distillation curves may vary widely between two fuels, the vapor pressures determined at one set of conditions for several fuels may not indicate the relative vapor pressures of the same fuels under widely different conditions.

The same problem that exists for vapor pressure exists for boiling point. The boiling point is defined as the temperature at which the vapor pressure of a liquid is equal to the ambient pressure. The normal boiling point is defined as the temperature at which the vapor pressure of the liquid is exactly equal to 1 atmosphere (1 standard sea level atmosphere or 760 mm Hg.). For pure substances the Clausius-Clapeyron may be used to estimate the change in boiling point with pressure. The boiling point depends upon the liquid-vapor volume. For purposes of standardization the "true" vapor pressure is probably the best choice from which to obtain boiling point data.

Some empirical relationships have been developed for conventional fuels that permit conversion of one measure of volatility to another.

Reid vapor pressure, for example, can be related to the ASTM distillation curve as follows:

$$P_R = S \left(\frac{a}{\rho_{60}t_{20} + b} + c \right) \tag{14}$$

36
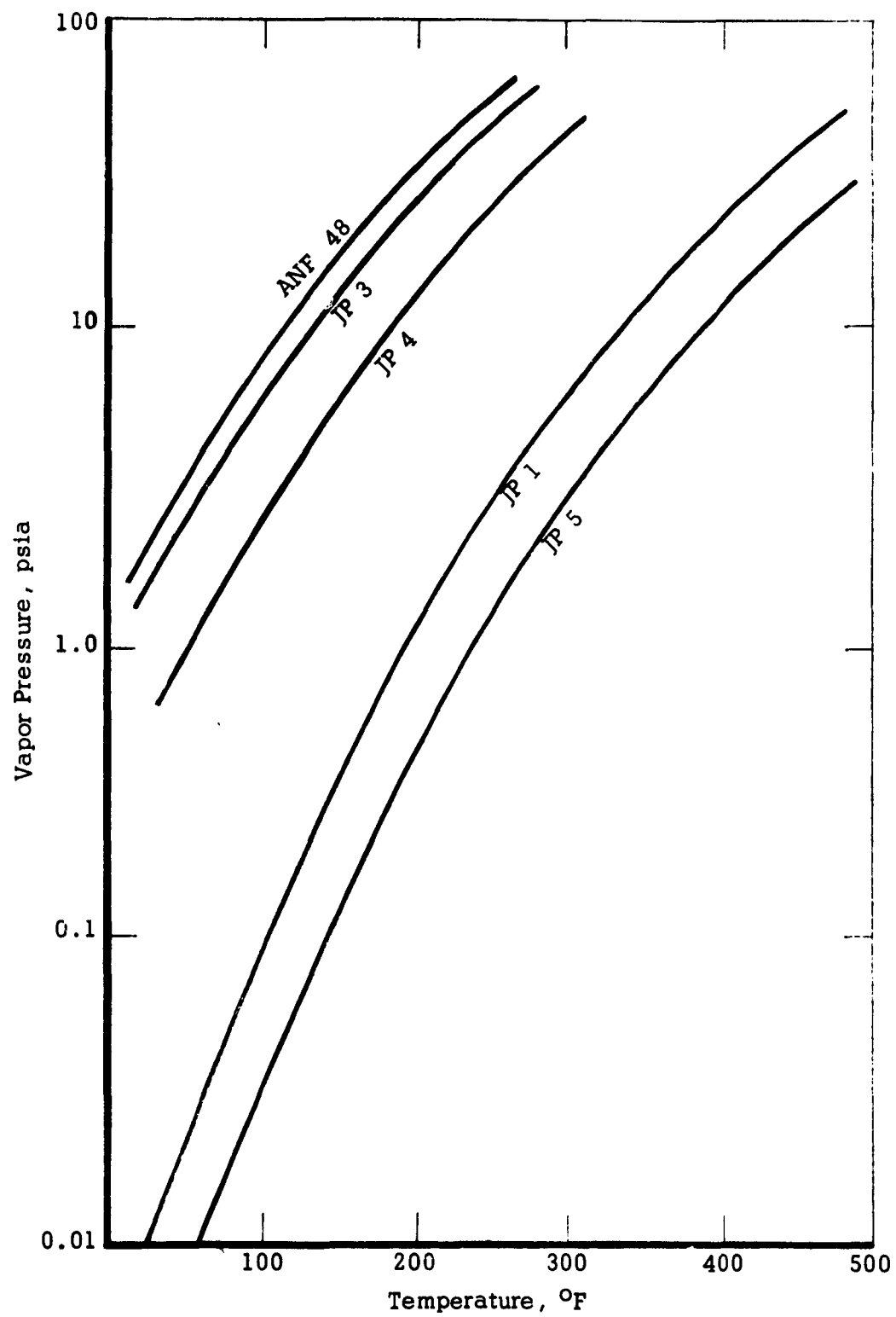
Figure 15. Vapor Pressures of Fuels

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where P_R = Reid vapor pressure, #/sq. in.

S = slope of ASTM distillation curve at the 10% evaporated point

$$S = \frac{t_{15} - t_5}{10} \tag{15}$$

$t_{20}, t_{15}, t_5 \ldots$ = temperature on ASTM distillation curve for 20%, 15%, 5% .... evaporation

ρ_{60} = density at 60°F of liquid fuel

a, b, c = constants which depend on fuel – listed below for three fuels

Fuel	a	b	c
Av. Gas	486	−50	−4.33
JP-4	114	−89	− .45
JP-3	46	−104	− .42

For mixtures of several fuels, the Reid vapor pressure can be obtained from the equation:

$$P_R = P_{R,1} N_1 + P_{R,2} N_2 \tag{16}$$

where P_R = Reid vapor pressure of mixture

$P_{R,1}, P_{R,2}$ = Reid vapor pressure of fuel 1, 2, etc.

N_1, N_2 = volume fraction of fuel 1, 2, etc.

The "true" vapor pressure at 100°F can be estimated from the Reid vapor pressure (determined at 100°F) by the following relationship:

$$P_{100} = P_R + 0.0223 P_R + \frac{0.0119 P_R S}{1 - 0.0368 P_R} \tag{17}$$

The Reid vapor pressure is not directly used in the calculations of fuel-air ratios involved in a hazard study. Since it is often used to characterize fuel volatility, however, it is useful to be able to convert Reid vapor pressure to actual vapor pressures. The relationship between Reid vapor pressure and the "true" vapor pressure at 100°F serves such a purpose. The Clausius-Clapeyron equation can then be used to obtain vapor pressures at other temperatures. Additional quantities needed for such a calculation are

the heat of vaporization for extrapolation of vapor pressure data and molecular weight for fuel-air ratio calculations.

Correlations of properties for conventional fuels are often accomplished through the use of various average boiling points. The most widely used average boiling point is the volumetric average since this quantity is readily obtained from the ASTM distillation curve. The volumetric average boiling is most precisely defined as:

$$t_v = \frac{\int_{t_i}^{t_f} V \, dt}{t_f - t_i} \tag{18}$$

where t_v = volumetric average boiling point

  V = volume distilled in ASTM test

  t_i = initial boiling point

  t_f = final boiling point

Since the required integration is often difficult to perform, approximate values may be obtained from the relation:

$$t_v = \frac{t_{10} + 2t_{50} + t_{90}}{4} \tag{19}$$

where t_{10} = 10% evaporated temperature

  t_{50} = 50% evaporated temperature

  t_{90} = 90% evaporated temperature

Another average boiling temperature is often used for more precise estimates of hydrocarbon fuel properties. This quantity, called the "mean average boiling point" can be correlated with the volumetric average boiling point and the slope of the ASTM distillation curve for the 10% fraction. The correlation curves are shown in Figure 16 (Ref 10) for the mean average, weight average and molal average boiling points. In many cases where order of magnitude estimates are satisfactory, the volumetric average boiling point can be used in place of the mean average boiling point.

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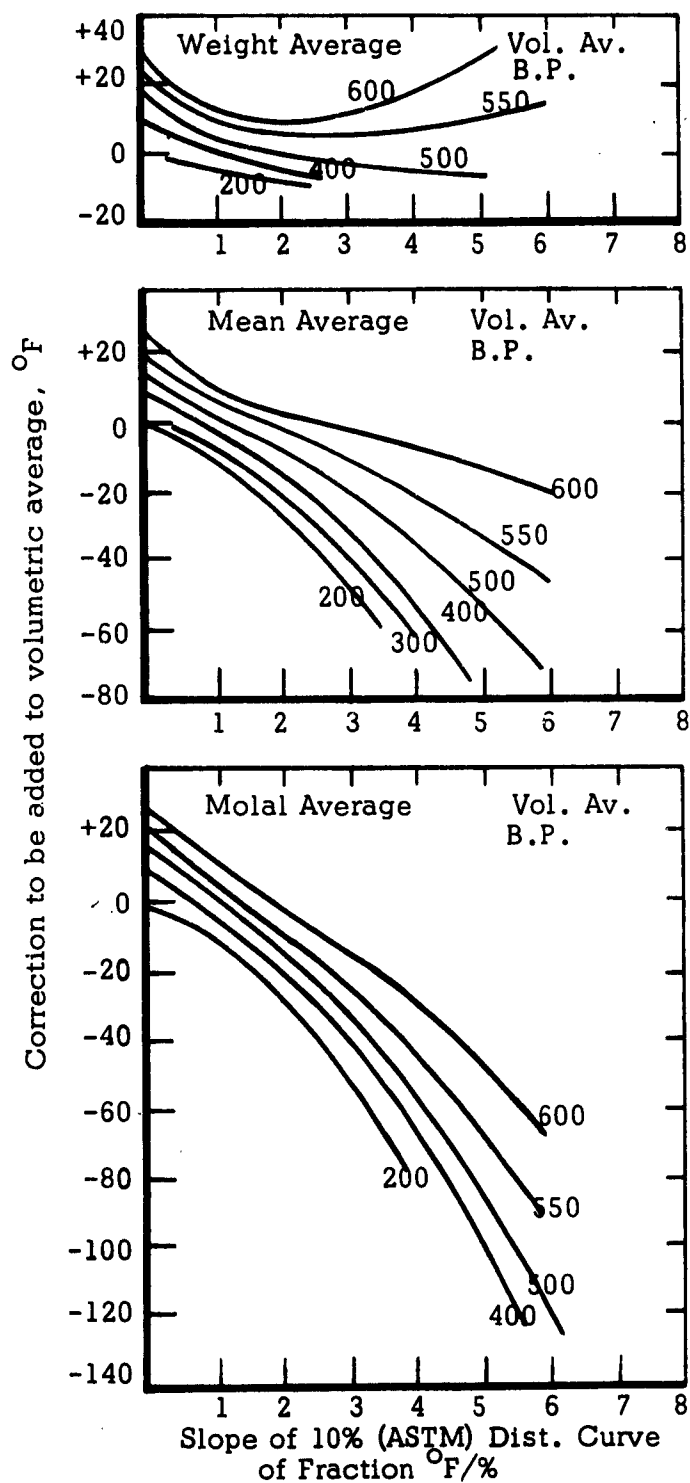
Figure 16. Average Boiling Point of Petroleum Fractions 10% (A.S.T.M.) Distillation

Courtesy of D. Van Nostrand Company, Inc.

In order to use the Clausius-Clapeyron equation for vapor pressure extrapolation, the heat of vaporization is required. The most accurate method of estimating heats of vaporization is through the use of the rule of corresponding states described in Ref 10. Simpler methods are often sufficient, however. A very crude method involves Trouton's rule which can be written

$$\frac{\Delta H_V}{T_B} = \Delta S_V \tag{20}$$

where ΔH_V = heat of vaporization

T_B = boiling point

ΔS_V = entropy of vaporization

For ΔH_V in Btu/lb and T_B in degrees Rankine, one finds that

$$\Delta S_V = 22/(M.Wt) \tag{21}$$

where the molecular weight (M.Wt) can be obtained from the correlation illustrated in Figure 17. The different lines represent different petroleum fractions. It is recommended for approximate calculations that the line III be used (data from Ref 10).

The variation of heat of vaporization with boiling point, obtained from pure hydrocarbon data, can also be used. A graph of this relationship is shown in Figure 18. The mean average boiling point would be used for mixed petroleum fuels to obtain an estimate of the heat of vaporization.

b. Density

A full discussion of the density of aircraft fluids is beyond the scope of the present report and is not particularly pertinent to the fire hazard problem. Fluid specifications often quote the specific gravity of the fluid or the API gravity. The API gravity quoted as degrees API is related to the specific gravity by the equation

$$^\circ API = \frac{141.5}{\rho_{sp}} - 131.5 \tag{22}$$

4.
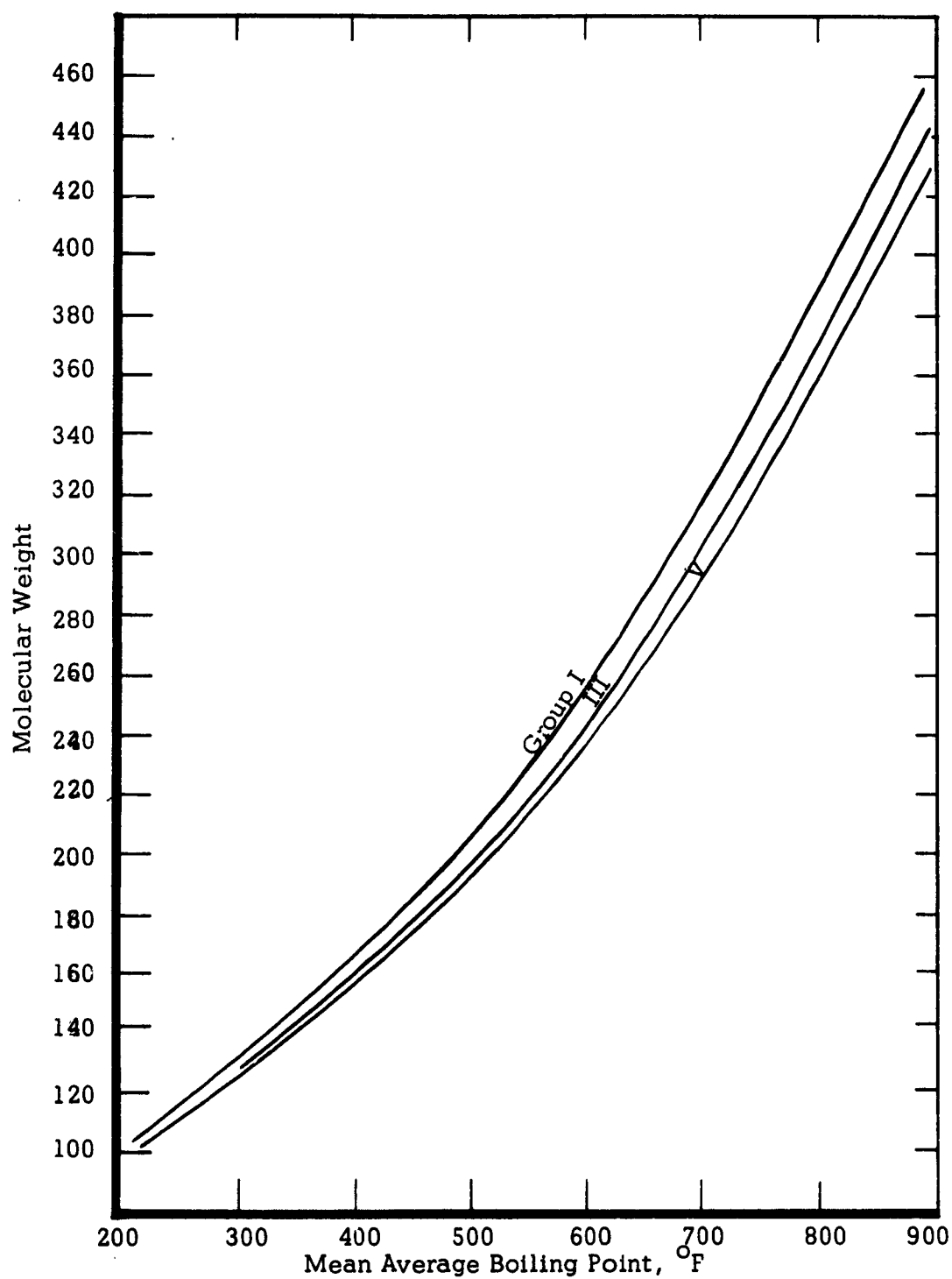
Figure 17. Molecular Weight versus Boiling Point Typical
Crude Fractions

Courtesy of D. Van Nostrand Company, Inc.
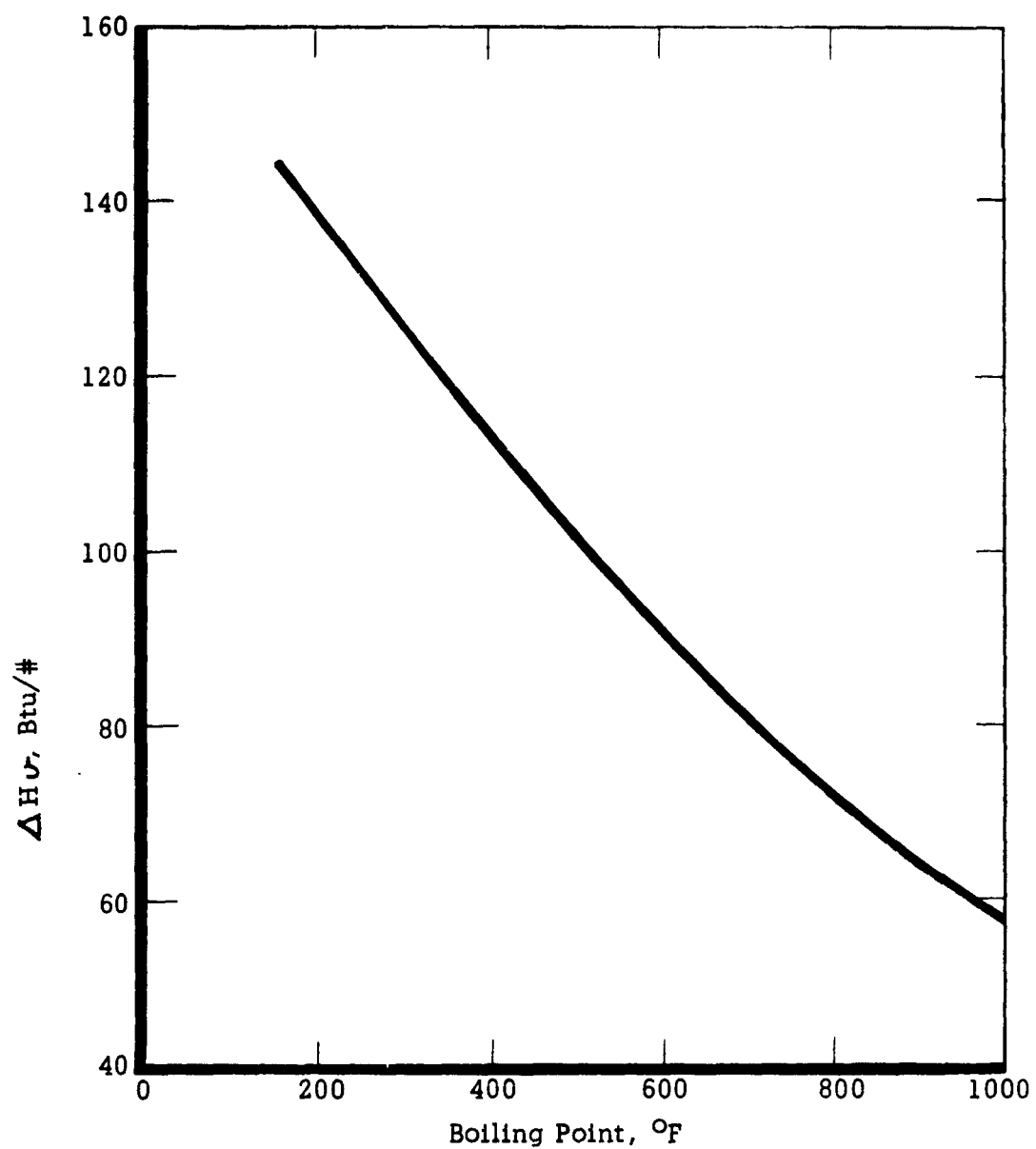
Figure 18. Heat of Vaporization versus Normal Boiling
Point for Paraffin Hydrocarbons

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where ^{O}API =   API gravity

   ρ_{sp} =   specific gravity at $60^{O}F$ compared to water at $60^{O}F$

The density can be obtained from the specific gravity by the relationships

$$\rho \left(\frac{lb}{cu\ ft} \right) = 62.43 \times \rho_{sp} \tag{23}$$

$$\rho \left(\frac{lb}{gal} \right) = 8.347 \times \rho_{sp} \tag{24}$$

The change of density with temperature can be determined from the relationship

$$\rho_t = \rho_{60} \left[1 + C_{ex} (60 - t) \right] \tag{25}$$

where ρ_t =   density at temperature t

   ρ_{60} =   density at $60^{O}F$

   C_{ex} =   coefficient of expansion (volumetric)

   t   =   temperature, ^{O}F

c. Compressibility

The change of density of a fluid with changes in temperature is due to the change in volume of a given weight of liquid with temperature. These changes are generally described in terms of an expansion coefficient and occasionally as a coefficient of compressibility. Heating a liquid under constant pressure conditions produces a change in volume. Such volume changes expressed as multiples of the initial volume for a fluid initially at $60^{O}F$ are illustrated in Figure 19 for a pressure of 1 atmosphere (0 psig). Fuel characteristics are described in terms of the molal average boiling point. A similar set of curves for 1500 psig is shown in Figure 20. These data permit estimation of the expansion of liquids in tanks and lines. The effect of pressure on the volume expansion is small, large pressure changes modifying the expansion only slightly. For example, a fuel with a molal average boiling point of $500^{O}F$ will show an expansion of 1.4 at $600^{O}F$ (starting at $60^{O}F$) for a pressure of zero psig and an equal expansion (1.4) at $665^{O}F$ for a pressure of 1500° psig.

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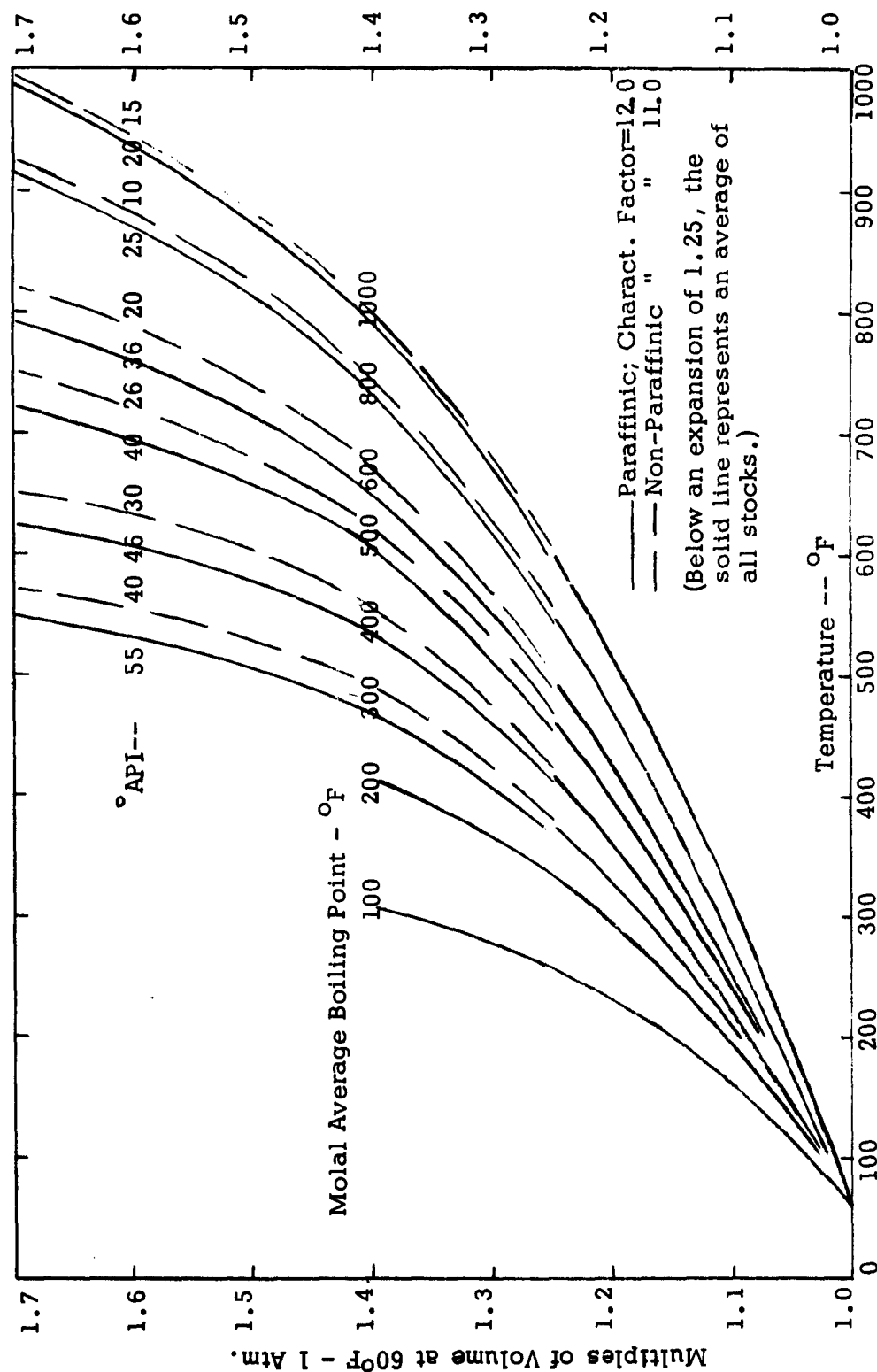
Figure 19. Thermal Expansion of Liquid Petroleum Fractions
0 Lbs./Sq. In. G.

Courtesy of D. Van Nostrand Company, Inc.
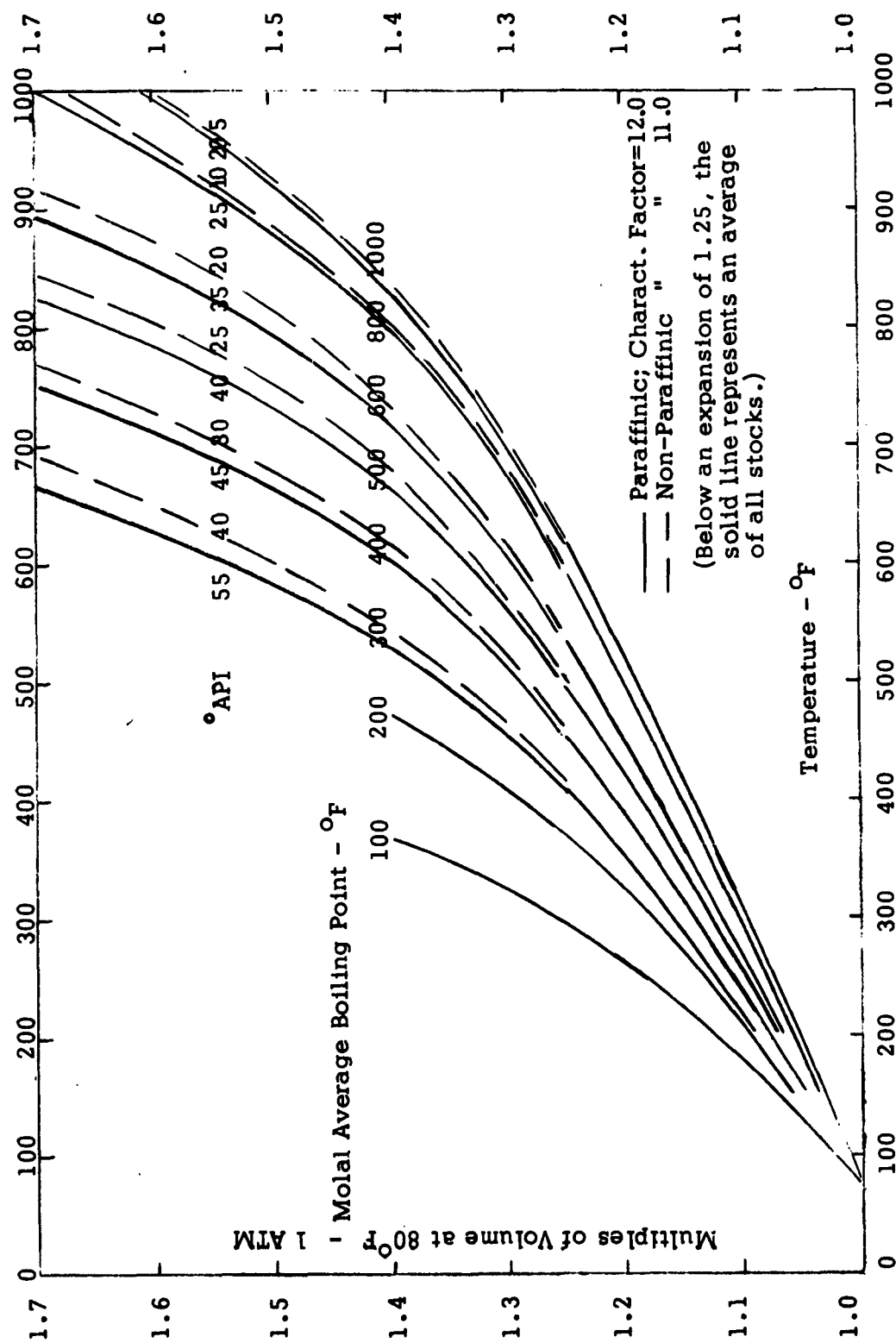
Figure 20. Thermal Expansion of Liquid Petroleum Fractions
1500 Lbs./Sq. In. G.

Courtesy of D. Van Nostrand Company, Inc.

The small compressibility due to pressure is an extremely important factor in hazard considerations. Using the same example cited above, a 65°F change in temperature (for a constant volume) will produce a change in pressure from 1 atmosphere to 100 atmospheres (0 psig to 1500 psig). This dramatic change in pressure for small temperature changes shows the ease with which bursting pressures can be developed for a totally confined liquid. A cross plot of the expansion data at a constant volume for a fuel with a molal average boiling point of 500°F showing the rapid change of pressure with temperature is given in Figure 21.

2. Hydraulic Fluids and Oils

The behavior of petroleum base hydraulic fluids follows the same general trends as do petroleum based fuels and no additional discussion is presented here. The correlations with boiling point can be extended to include these higher molecular weight fluids.

The requirement of high temperature stability for the hydraulic fluids used on the supersonic transport as well as the continued search for less flammable and more stable hydraulic fluids has resulted in several new fluid types which would have different characteristics than the hydrocarbon fluids discussed previously. Unfortunately, these fluids differ greatly in their chemical characteristics so that it is not usually possible to prepare generalized correlations. Furthermore, many of these fluids are sufficiently new that extensive data on their properties are not available. Nevertheless, a brief summary of some of the properties of hydraulic fluids is presented here.

The various Skydrols are hydraulic fluids widely used in subsonic aircraft. These fluids have been of interest because of their fire resistant properties. The use of Skydrol type fluids for the supersonic transport is a matter for design compromise between its fire resistance and satisfactory performance record and its upper thermal limit of about 225°F. Skydrol fluids would thus require that the complete hydraulic system be maintained at temperatures below 225°F.

A comparison of the vapor pressure of two Skydrol type fluids and a petroleum base hydraulic fluid (MIL-H-5606) is made in Figure 22.

The kinematic viscosities of these fluids are compared in Figure 23 from Ref 11.

Some of the other fluids under consideration for high temperature applications include (Ref 12).

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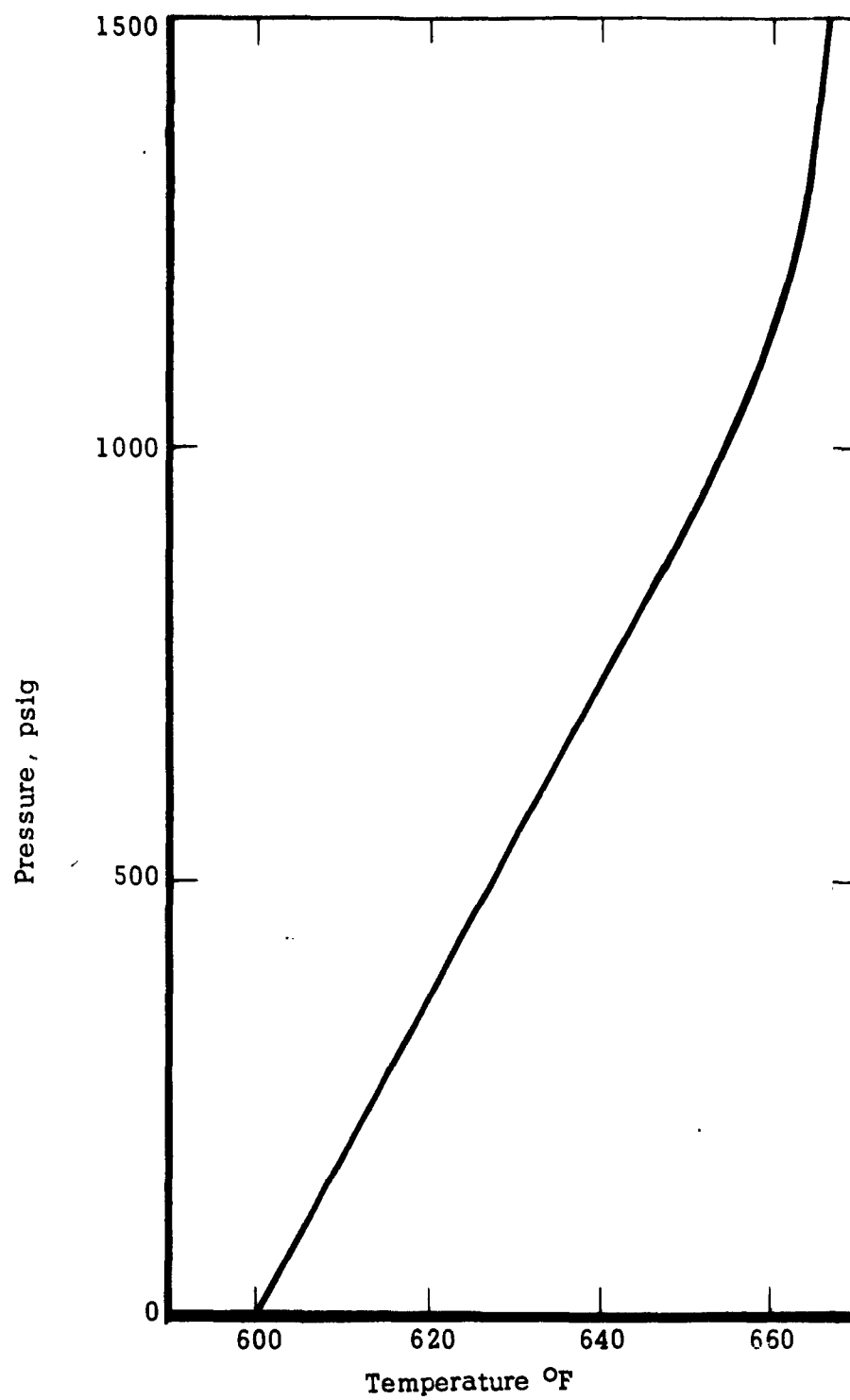
Figure 21. Variation of Liquid Pressure with Temperature
at Constant Volume

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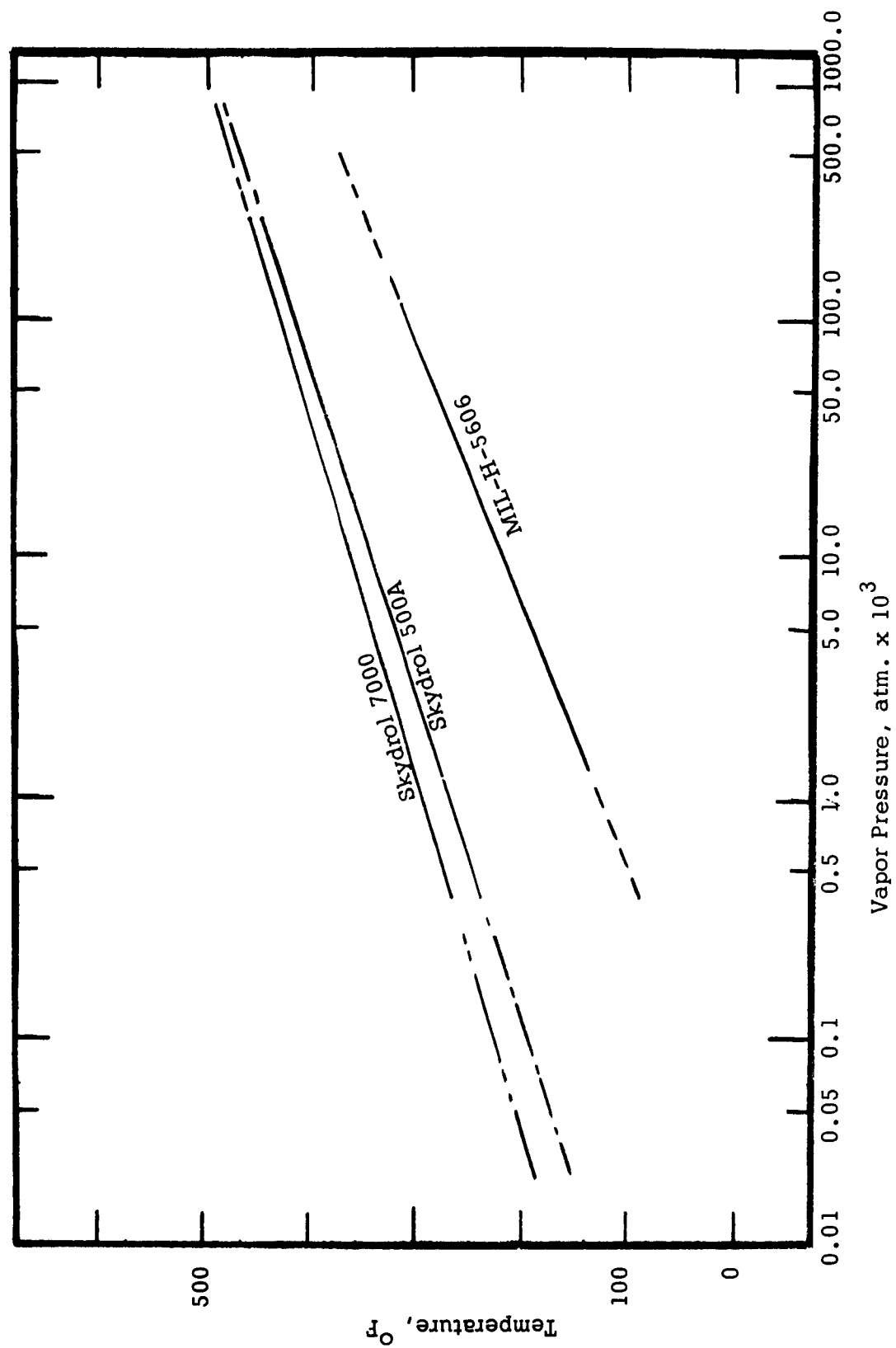
Figure 22. Vapor Pressure Skydrol 500A, Skydrol 7000 and MIL-H-5606
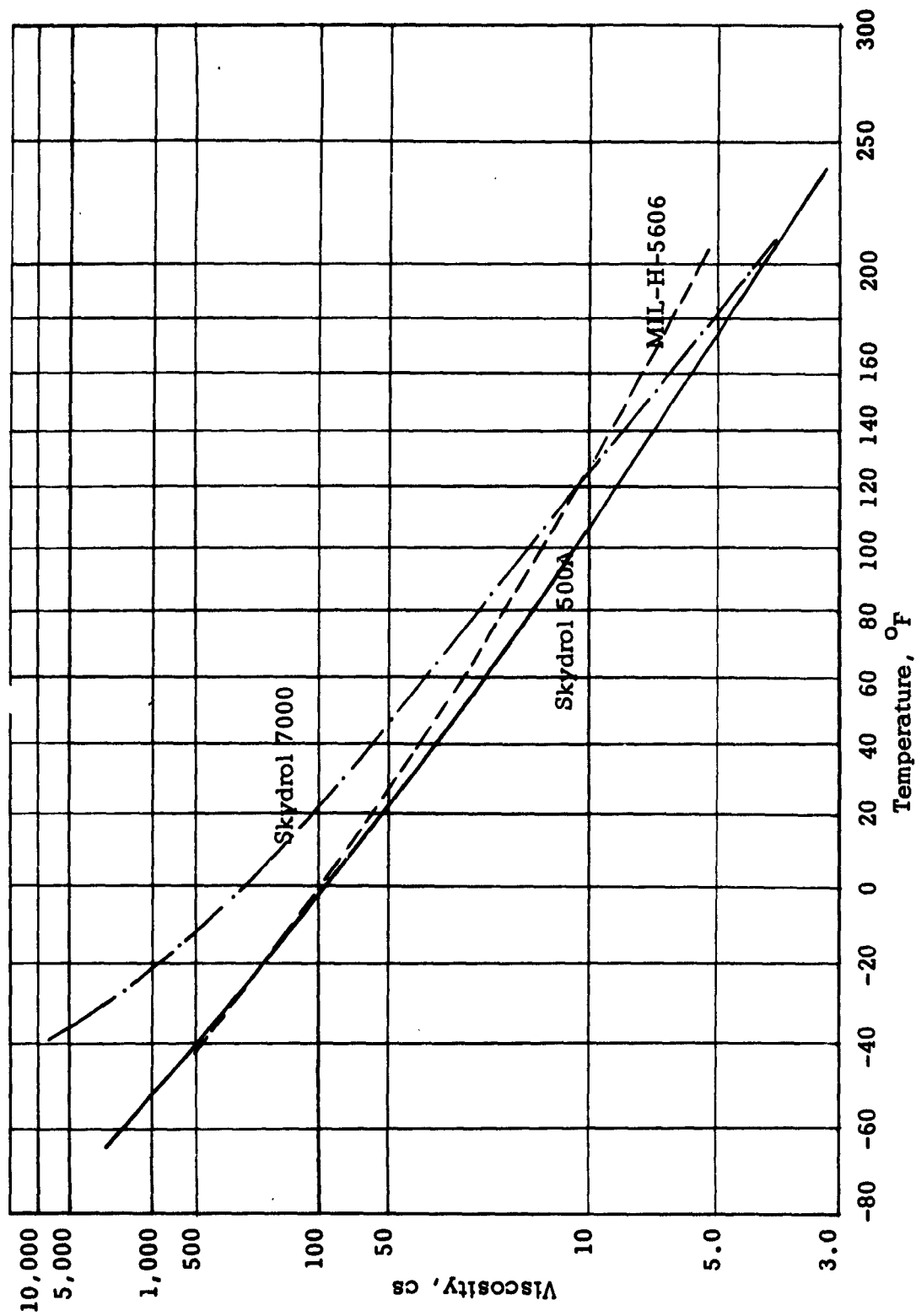
Figure 23. Kinematic Viscosity of Skydrol 7000, Skydrol 500A and MIL-H-5606

MLO 59-98	50-50 blend of phenyl methyl silicone and ester of trimethylol propane
MLO 57-637	Dyphenyldi-n-dodecylsilane
MLO 56-843	Chlorinated phenyl methyl silicone
MLO 59-692	Bis (phenoxy phenoxy) benzene
MLO 60-294	Deep dewaxed mineral oil with tricresyl phosphate, phenyl-x-naphthyl amine and DC 200
QF-258	Phenyl methyl silicone
XF-1-0270	Chlorinated-fluorinated silicone
XRM-142A	Synthetic hydrocarbon
XRM-146A	Synthetic hydrocarbon
MLO-7277	Super Refined Mineral Oil
MLO-7688	Super Refined Mineral Oil
F-50	Chlorinated silicone
O-70	Polysiloxane

Viscosities for a number of these fluids at several temperatures are summarized in Table 3.

Although some of the fluids show very little variation in viscosity with the continued use at 550°F, others show a decrease in viscosity with time. The decrease in viscosity can probably be associated with the break-up of larger molecules to form smaller ones. One would expect then, that the properties of the fluid will change with time including such significant variables as vapor pressure, flash point, etc. These changes will be discussed in connection with the combustion properties of various fluids and specific hazards.

Many of the same comments and in fact many of the same fluids are applicable to lubricating oils for the supersonic transport. The high temperature oils are generally of the silicone and fluorocarbon type discussed in connection with hydraulic fluids. The hydrocarbon oils follow the same relationships shown for hydrocarbon fuels, although the distillation data are usually not

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Table 3. Viscosities of Hydraulic Fluids

	Viscosity, centistokes		
Fluid	$100^{\circ}F$	$210^{\circ}F$	$500^{\circ}F$
MLO 59-98	62	14	
MLO 57-637	37	6	
MLO 56-843	58	19	
MLO 59-692	360	13	
MLO 60-294	14	3	0.7
QF-258	59	20	
Skydrol 500A	10	3	
Skydrol 7000	15	4	
MIL-H-5606	14	5	
XF-1-0270			3
XRM-142A			.9
XRM-146A			1
MLO-7277			1
MLO-7688			3
F-50			3
0-70			1

obtained since they are not included in specifications. Vapor pressures can often be deduced from other properties such as the flash point. This will be discussed in detail in the section dealing with combustion and flammability.

The volatility characteristics of hydraulic fluids and oils are an important part of the fire hazard evaluation. An empirical relation to assist in the estimate of vapor pressure is illustrated in Figure 24.

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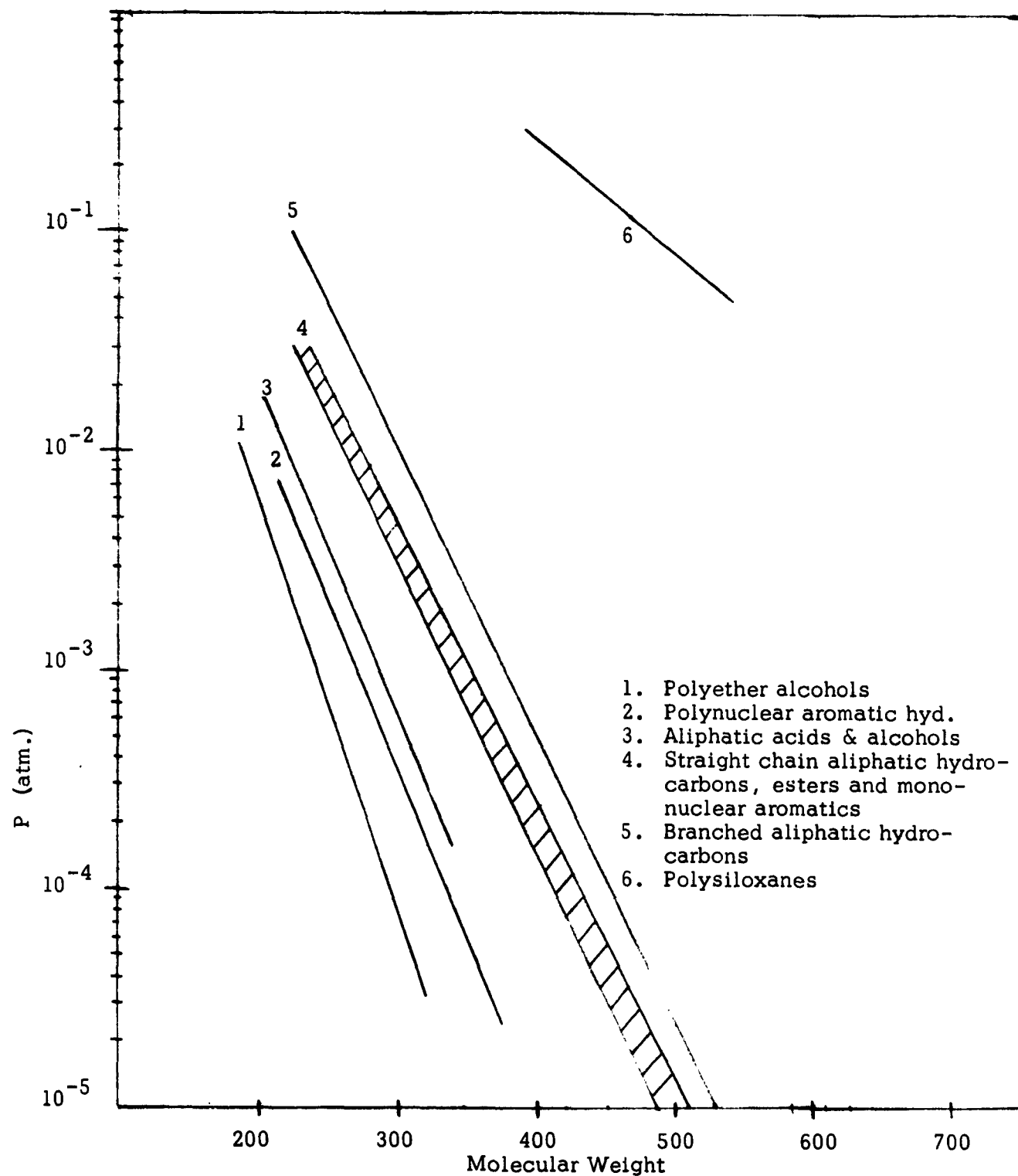
Figure 24. Variation of Vapor Pressure with Molecular Weight
(from Industrial and Engineering Chemistry, December 1950; page 2425)

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D. COMBUSTION PROPERTIES

This section represents a summary of the combustion data pertinent to the fire hazard problem. Most of this section of the report is devoted to the presentation of the data considered to be most pertinent to the supersonic transport fire hazard problem. The interpretation of the data in terms of specific fire hazards is treated in a subsequent section. This section has been subdivided into conventional combustion headings for convenience in presentation.

1.   Thermal Ignition

The exposure of a flammable-air mixture or a flammable in contact with air to a source of heat can lead to ignition of the flammable at temperatures above some critical value. Below this critical value of temperature, chemical reactions may occur leading to decomposition and/or partial oxidation of the flammable, but an explosion or flame is not observed. Ignition or the observation of flame is usually detected by a rapid increase in temperature or pressure or the emission of light or all of these simultaneously. The temperature at which these criteria of ignition are observed is strongly dependent on the experimental method so that it is difficult to define an "absolute" ignition temperature, characteristic only of the chemical composition of the system. For this reason thermal ignition temperatures have little meaning unless the experimental procedure is specified. Strict attention to experimental details can lead to repeatable ignition temperatures by different investigators.

One of the reasons for the difficulty in defining a unique ignition temperature is the fact that the properties of the folume element of gas which first ignites are not measured. Rather, the temperature usually measured is the temperature of an environment, such as furnace wall, which results in some critical condition at some unknown and unspecified location within the flammable-air system. Since heat transfer characteristics affect local temperatures within the system, the apparatus can affect the results by influencing heat transfer rates to and from various zones in the system. In some experiments composition gradients also exist within the system so that mixing can also affect the value of the temperature reported as the ignition temperature. Unknown catalytic effects of surface may also influence the results.

Presumably ignition occurs when the chemical reactions produced by raising the temperature of the reaction system release heat at a more rapid rate than heat is lost from such a zone. The result is a further increase in temperature, increased chemical reaction rates, and ultimately ignition or explosion of the mixture. It is entirely possible, although far from a demonstrable fact, that if the temperature, composition, catalytic effects and pressure of the zone which first participates in a rapid temperature rise could be measured, the variations in ignition temperature with experimental method would no longer exist. Such an experiment is difficult to conceive, however. First, the insertion of probes into the

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flammable-air system immediately alters the local environment. Second, the proper location for such a measurement is not known in advance and, coupled with the first problem, such a location would be affected by the presence of a probe.

The ignition temperature observed also varies with the time between the exposure of the flammable-air system to the specific temperature and occurrence of ignition – in other words the ignition temperature varies with ignition delay. More will be written on this subject later. At this point it will be sufficient to state that, in general, ignition temperatures increase as the time to ignite decreases. It is not clear, however, whether the higher temperatures associated with shorter delays represent a fundamental property of the system or whether higher temperatures merely permit a critical state, if one exists, to occur in a shorter time.

Interpretation of ignition temperature data is thus reduced to the problem of relating specific experimental results to the hazard situations to which they are most applicable.

The interpretation of the data to be presented will be facilitated by a discussion of the phenomena which occur when a fuel-air mixture is heated. A number of different phenomena may occur either in sequence or simultaneously. It is possible to classify the principal events into three different categories:

- a. Oxidation
- b. Cool flames
- c. Normal flames

These three regimes are illustrated in Figure 25, Ref 13. Although each of the three zones may contain additional subzones due to differences in chemical reaction, nature of cool flame, etc., these areas represent the major events.

a. Oxidation

The zone indicated as oxidation is also often called slow combustion, low temperature combustion or pre-ignition. It involves a chemical reaction involving, usually, the evolution of heat. It differs from a flame in several important respects. Principally, it is not self-propagating. This means that a heated zone in one region of a fuel-air mixture may cause oxidation to occur locally but the oxidation will not progress to colder regions. Usually other properties generally associated with a flame, such as light emission, are also absent and the pressure and temperature rise is not as pronounced as those generally associated with flame phenomena. As will be shown, the oxidation process may lead to a flame, however. The oxidation process consists of the combination of the fuel, or specific

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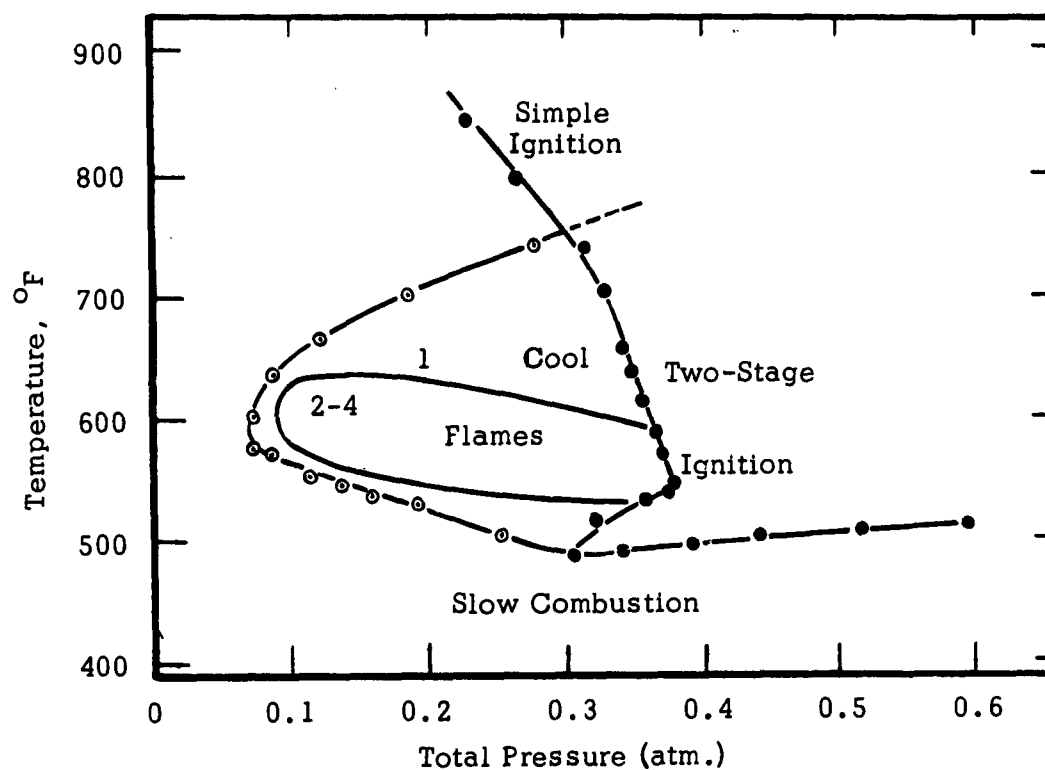
Figure 25. Conditions of Temperature and Pressure for
Combustion in Butane-Oxygen Mixtures
Containing 50 Percent Butane
(The numbers shown indicate the number
of cool flames observed.)

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components in a mixture, with oxygen to form chemical species containing oxygen.

The factors which govern the rate of such oxidation reactions are the temperature and the mixture composition. Unlike flame processes, however, these oxidation reactions do not necessarily have composition limits. Although the reactions are often quite complex, the dependence of the rate of reaction on temperature and composition can be illustrated by an Arrhenius type of expression:

$$\text{Rate} = A \, C_{fuel}^{m} \, C_{oxygen}^{n} \, e^{-E/RT} \tag{26}$$

where   C   = concentration

A   = constant

E   = activation energy

It is seen that the rate of reaction decreases as the oxygen concentration decreases but that the rate does not become zero until either the fuel or oxygen concentration reach zero. Unlike flame properties there is no critical reaction rate which must be exceeded for the oxidation to occur, hence one may observe such reactions under conditions where extremely small oxygen concentrations exist (or fuel concentrations), well beyond the usual flammability limits.

The problem of low temperature oxidation has not been of concern in terms of aircraft hazard evaluations for conventional aircraft since the low temperature environment precluded extensive reaction and minimized the follow-on effects, such as ignition, which can occur at higher temperatures. The temperature environment of the supersonic transport, including tank wall temperatures in excess of 500°F and fluid temperatures of the order of 250°F is in a region where extensive oxidation can occur and in which transitions from oxidation reactions to flames have been observed. A brief description of some of the experimental observations may assist in relating the phenomena associated with low temperature oxidation to specific problem areas of the supersonic transport.

Oxidation reactions can be noted at quite low temperatures for some of the more reactive hydrocarbon types such as olefins. Cyclohexane, for example, has been studied at temperatures from 59°F to 104°F (Ref 14). Liquid cyclohexane was exposed to air at various temperatures and the rate of oxygen absorption was observed. The rate of oxidation was independent of the partial pressure of oxygen above a level of 40 mm.

The rate of absorption of oxygen at 104°F varied from 0 to 1.75×10^{-2} millimoles of oxygen absorbed per hour for variations of cyclohexane liquid volume from 0 to 1.0 milliliters. A millimole of oxygen corresponds to .032 grams.

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While the oxidation data cited are not immediately pertinent to supersonic transport conditions, the observation of reaction has a strong relevance to the fire hazard problem in the supersonic transport.

The products of oxygen absorption include hydroperoxides, compounds of the type ROOH as well as other reactive compounds. The accumulation of such compounds could affect the ignition temperature of the fuel in a manner which would lead to decreasing ignition temperature with time. The results of such low temperature oxidation processes could thus affect the probability of a normal ignition process occurring. There are not sufficient data available to predict the effect of such low temperature oxidation reactions on spontaneous ignition temperature.

The rate of oxygen absorption will be a function of temperature and, in most cases, will vary exponentially with temperature. In a system where heat transfer may be a relatively slow process, oxidation reactions proceeding at a reasonably rapid rate of 250°F compared to 100°F may result in local increases in temperature which may lead to ignition of a normal flame. This is the mechanism, for example, of the spontaneous ignition of oily rags, etc. This phenomenon will be discussed in more detail later.

The gas phase oxidation reactions are probably even more pertinent to the supersonic transport fire hazard problem than the liquid phase reaction described in the previous paragraphs. The general characteristics of such gas phase reactions are quite similar to the liquid phase oxidation in a number of important aspects. Both types of reaction can occur in compositions of fuel and air well outside of the normal flammability ranges. In fact, these reactions can occur if only very small amounts of oxygen are present. Both types of reaction lead to the evolution of heat and the formation of chemically reactive intermediates and can lead to normal flames under conditions which would not usually be expected to cause ignition.

Propane oxidation has been studied by a number of investigators. Typical of the results are the data of Ref 15 which shows appreciable oxidation of propane at a temperature of 680°F. In the cited work, a mixture containing 13.1 per cent oxygen showed almost complete reaction of the oxygen at 680°F in about 4 seconds. The principal products of reaction were propylene, carbon monoxide, methyl alcohol and water. Similar results are reported in Ref 16.

The higher molecular weight hydrocarbons show the same type of oxidation behavior at lower temperatures. For example, n-Heptane shows appreciable peroxide formation in the temperature range of 550-575°F (Ref 17).

No attempt has been made to summarize all of the data in the literature on slow oxidation of hydrocarbons. The data are generally not in the range of interest for the conditions pertinent to the supersonic transport.

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Furthermore, there is often a strong dependence of the actual rates of reaction observed on the experimental method, particularly surface effects.

It appears unlikely that the presence of these oxidation reactions by themselves will constitute a hazard. The pressure rises associated with such reactions are generally quite small and the temperature rise is insufficient to produce a damaging effect. The hazard associated with the low temperature oxidation reactions is principally associated with their effects on related combustion properties. The formation of peroxides and other reactive species as a result of these oxidation reactions may change the ignition characteristics of the system. The oxidation reactions may change the temperature and pressure sufficiently to cause ignition of a cool flame or even, under some conditions, a normal flame. The latter, in fact, is one of the ignition mechanisms proposed in various regions of temperature and pressure.

An indication of the change in pressure which can occur during slow combustion can be obtained for pentane-oxygen mixtures from the following table:

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Table 4. Pressure Increase Due to Slow Oxidation*

Pentane - Oxygen

Temp $^\circ$F	Initial Mixture		Pressure Increase atm.
	Pressure atm.	Pentane % (Volume)	
500	0.999	19.9	0.1975
	0.758	20.5	0.1460
	0.768	27.0	0.1317
	0.656	20.6	0.1223
	0.667	30.3	0.1092
	0.512	25.5	0.0895
	0.512	32.2	0.0803
	0.524	50.6	0.0553
	0.396	31.2	0.0645
	0.401	49.0	0.0434
	0.263	51.5	0.0263
	0.126	30.6	0.0211
518	0.794	13.7	0.1645
	0.538	15.5	0.1092
	0.383	32.9	0.0645
536	0.191	23.9	0.0356
	0.200	40.2	0.0276

Ref 18 *Prettre, 3rd Symposium

The results were found to be independent of the size of the reaction chamber when the chamber had a diameter in excess of 1 inch.

Temperature rises are more difficult to generalize since the increase in temperature is so strongly dependent on the specific reactions taking place and the rates of these reactions. It may be safely assumed, however, that corresponding temperature rises occur during the increase in pressure.

b. Cool Flames

Examination of Figure 25 shows a region separating the oxidation zone from a region called cool flames. Like the oxidation process, the cool flame represents a chemical reaction involving partial reaction of the fuel with oxygen and the liberation of heat. The cool flame, however, represents a self-sustaining reaction which will propagate through a mixture once ignited. The cool flame also emits light and hence has the characteristics usually associated with a flame.

A cool flame can be the result of a process which begins as an oxidation reaction. Referring again to Figure 25, if the oxidation process produces an increase in either temperature or pressure, the conditions necessary for cool flame propagation may be reached although the temperature and pressure of the original environment were outside the cool flame region. This is, in fact, one of the common methods by which cool flames originate. The heat generated by the oxidation reactions produces a local temperature rise which initiates the cool flame. The oxidation process, by itself, can only continue without leading to a flame if the heat generated is too small to raise the temperature to a critical value or if the heat transfer from the system is sufficiently large so that essentially isothermal conditions are maintained.

Changes in the environment can also lead to the formation of cool flames. Assume an oxidation occurring at a temperature above the cool flame limit but at a pressure below the cool flame limit. An increase in pressure as would occur during a normal descent could change the conditions to those appropriate for cool flame propagation.

Cool flames have been observed in mixtures containing as much as 95% hydrocarbon (Ref 19). Some typical cool flame boundaries for pentane are illustrated in Figure 26, from data of Ref 18. The variation of the cool flame boundary with pressure and composition at three temperature levels is illustrated in Figure 27 and the variation of the cool flame boundary temperature with composition for three levels of pressure is shown in Figure 28.

The boundaries between oxidation and cool flames shown for pentane are typical of those found for most hydrocarbons. Higher molecular weight hydrocarbons display the same behavior at somewhat lower temperature

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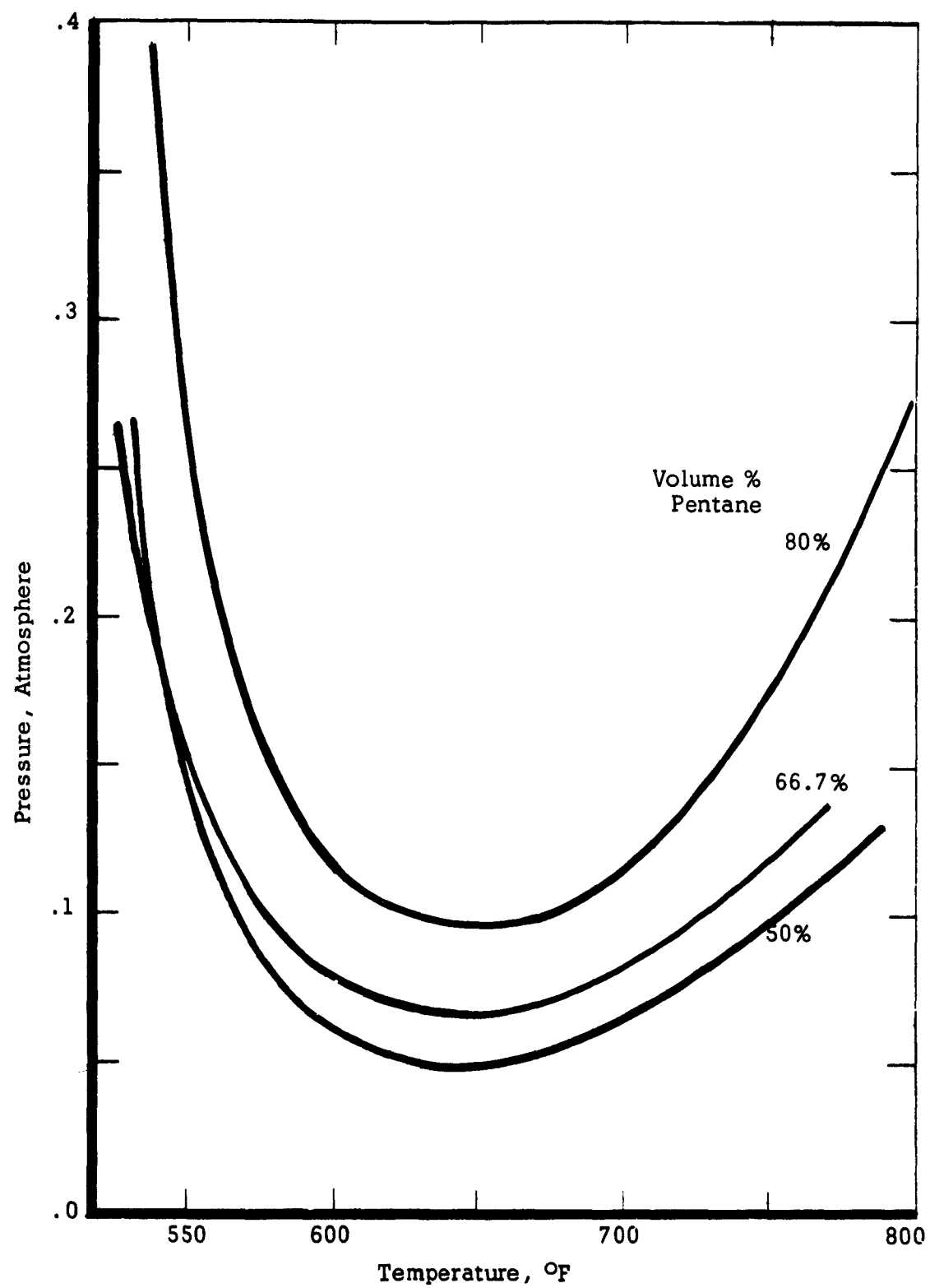
Figure 26. Cool Flame $C_5H_{12} - O_2$
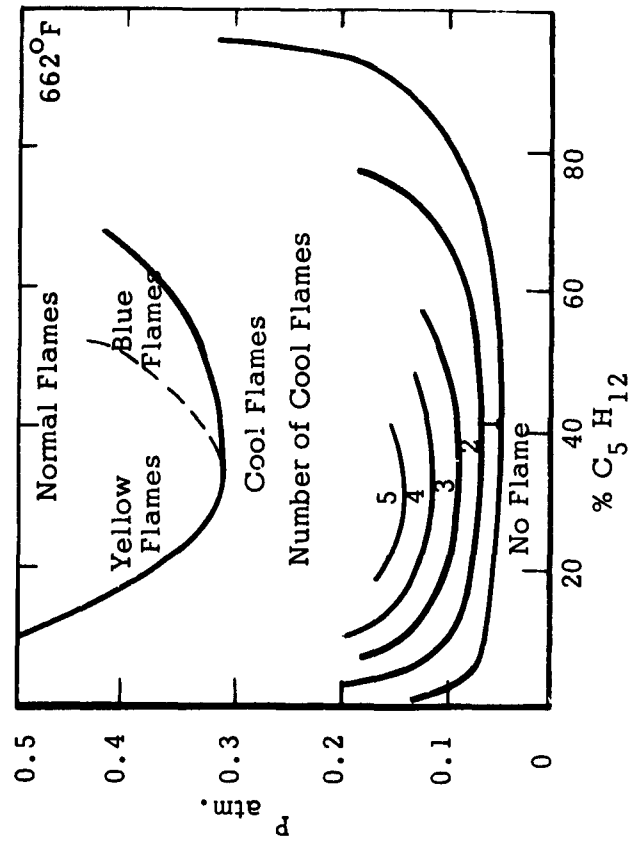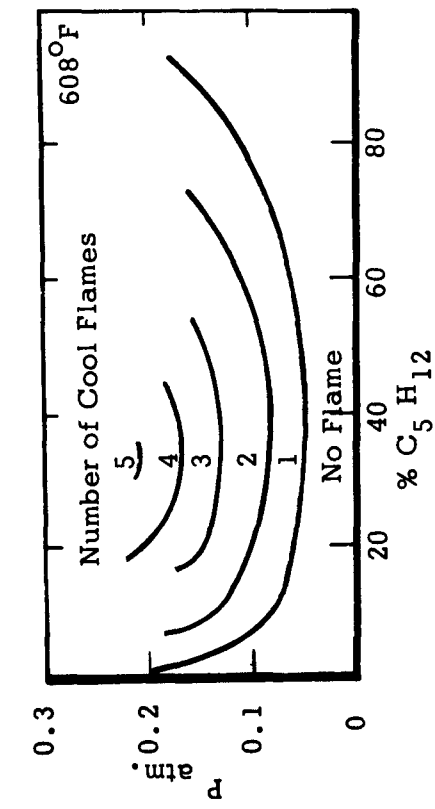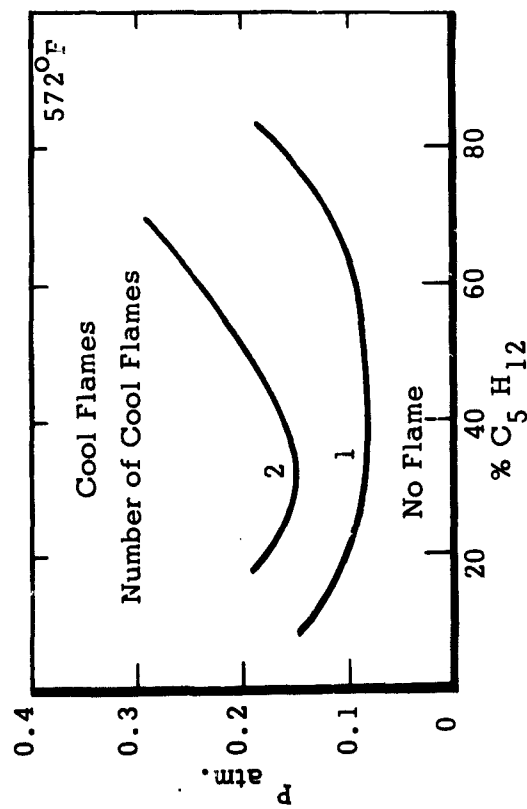
Figure 27. Variations of the Cool Flame Boundary with Pressure and Composition
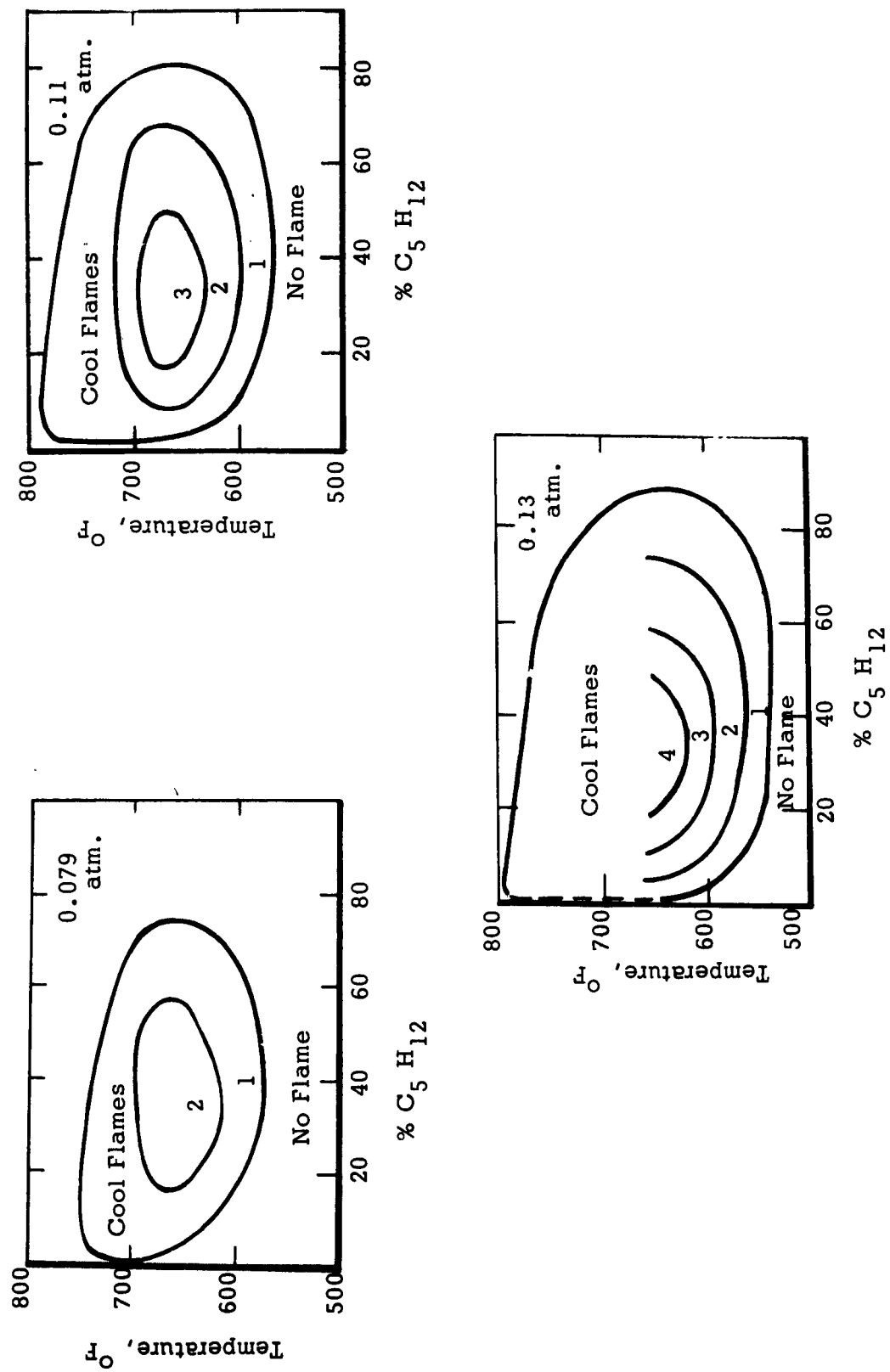
Figure 28. Variations of the Cool Flame Boundary Temperature with Composition
(Numbers indicate number of cool flames observed.)

levels, cool flames being observed at temperatures as low as 400-450°F. In fact, many of the ignition temperatures reported in the next section probably involve cool flames.

Cool flame ignition temperatures have been measured for three JP type fuels as a function of pressure. The observed ignition temperatures for both cool flames and normal flames are illustrated in Figure 29, for JP-4, JP-5 and JP-6 (Ref 20). In order to show a better comparison with the previous discussion involving Figure 25, the data for JP-5 have been replotted in Figure 30. The similarity is evident. Of particular interest is the relative insensitivity of the cool flame ignition temperature to decreases in pressure (or increases in altitude) between 1 atm and 0.2 atm or from sea level to altitudes approaching 40,000 feet. Above this altitude or below the corresponding pressure there is a slow increase of cool flame ignition temperature with decreasing pressure.

The region to the left of the cool flame ignition curve in Figure 29 and below the cool flame ignition curve in Figure 30 has been labelled "No Ignition." In Ref 20, this region has been called "No Reaction." It should be observed, however, that this region corresponds to the oxidation or slow combustion region of Figure 25 and that non-flame reactions could occur although an ignition would not be observed. The method of detection used would not detect such reactions since a visible change would not occur and the changes in either pressure or temperature would be relatively small, particularly if the observations were made over a relatively short period of time.

Additives have a very pronounced effect on cool flames. Tetraethyl lead, for example, represses the luminous low temperature oxidation reactions in hydrocarbons and cool flames do not appear at all (Ref 21). Some typical examples of the effect of tetraethyl lead on oxidation reactions and cool flames are presented in Table 5.

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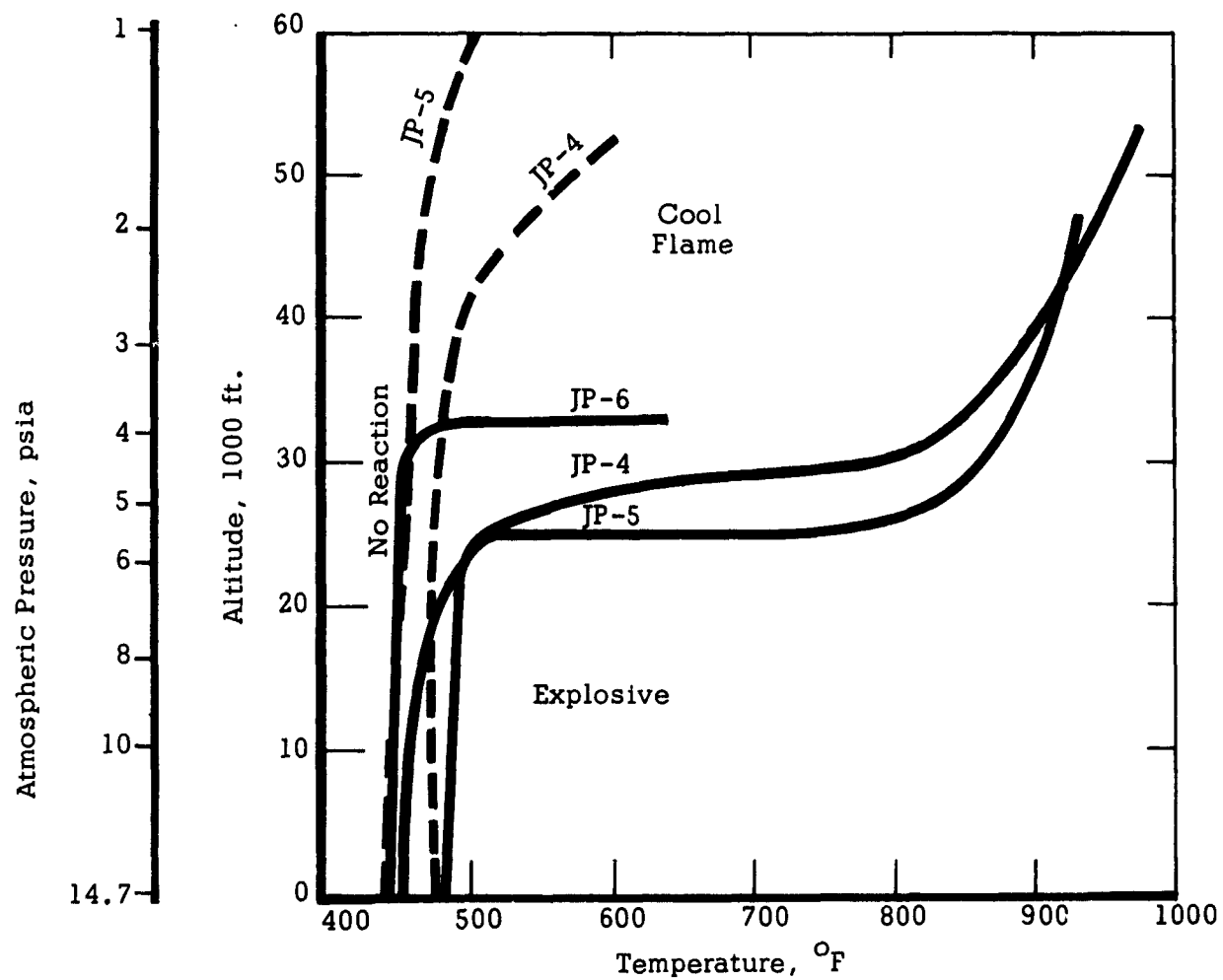
Figure 29. Spontaneous Ignition Reaction
Zones for JP-type Fuels
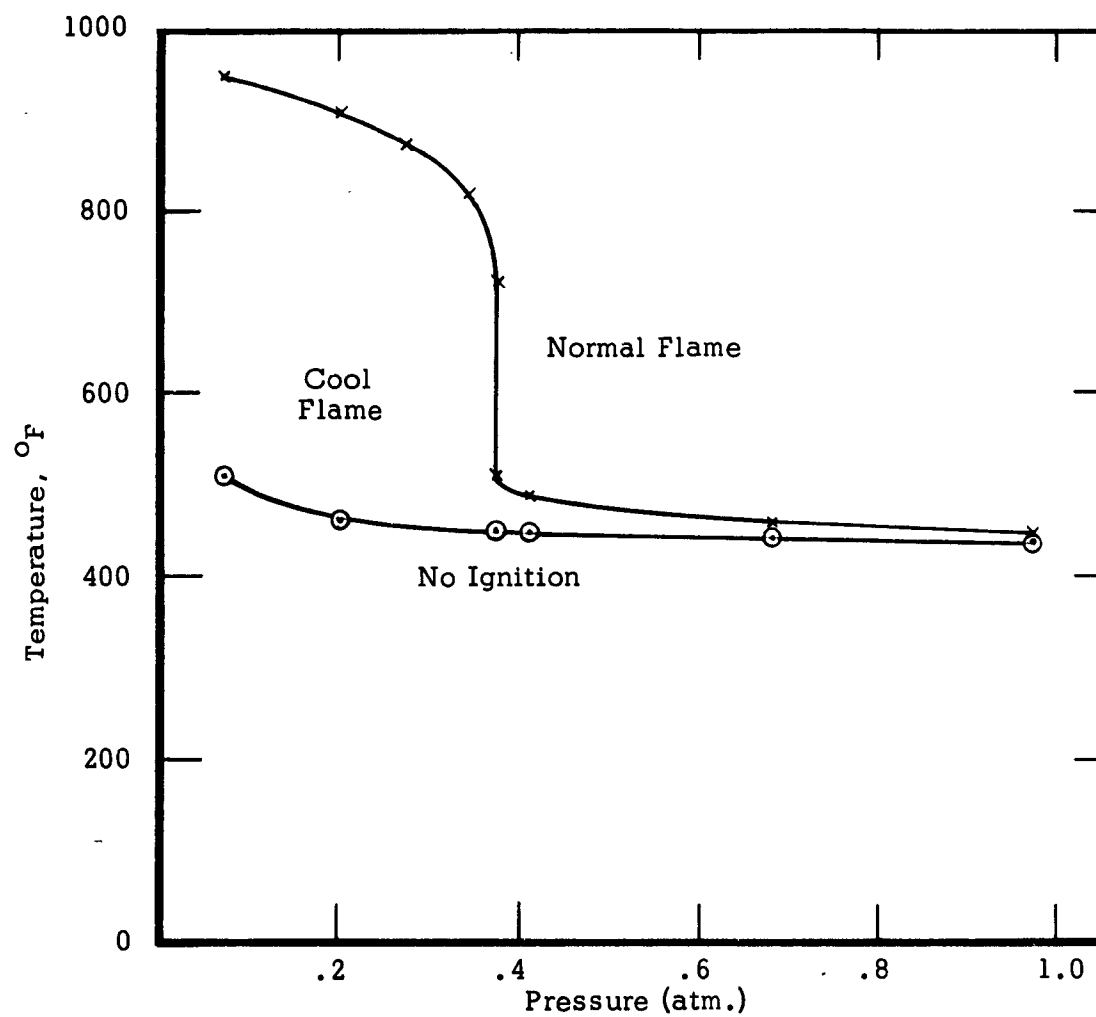
Figure 30. Ignition Zones for JP-5 as a Function of Pressure

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Table 5. Effect of Tetraethyl Lead on Hydrocarbon Ignition

Fuel	%TEL	Minimum Initiation Temperatures °F				
		Luminescence		Cool Flames		S.I.T.
		θ_1	θ_2	t_1	t_2	
Pentane	0	430	464	500	518	1238
	0.4	549	626	No Flame		No Ign.
Hexane	0	428	471	491	518	1242
	0.4	536	554	No Flame		1378
	0.6	635	698	No Flame		1384
Heptane	0	410	450	498	516	1267
	0.4	509	518	No Flame		1366
	0.6	572	608	No Flame		No Ign.
	0.8	680	761	No Flame		No Ign.

θ_1 Temperature at beginning of luminescence

θ_2 Temperature of brilliant luminescence

t_1 Beginning of cool flames

t_2 End of cool flames

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Spence and Townend (Ref 22) also point out the inhibition of lead tetraethyl over the entire ignition range and of NO_2 in the low temperature or cool flame range. In the high temperature range characteristic of normal flame ignition, NO_2 acts as an ignition promotor.

Various amines have also been found to affect the cool flame ignition characteristics of fuel-air mixtures. The effect of amines on ignition is illustrated in Figure 31 for an ether-oxygen mixture. Although specific data for hydrocarbon-air mixtures was not found, similar effects should be observed. Again, the cool flame region appears to have been completely eliminated and, over the entire range, the ignition temperatures have been increased (Ref 23).

The use of additives, by decreasing the rate and extent of reaction, should also reduce the pressure rise associated with cool flame propagation. No data were found which related pressure rise to inhibitor concentration for practical fuels. There are data, however, on the effect of diluents and reduced pressure on the pressure rise associated with cool flame propagation.

As a basis for comparison, pressure rise as a function of initial pressure (or altitude) are plotted in Figure 29 from Ref 20. To illustrate the significance of the pressure rise on tank pressure, selected points are compared in Table 6.

Table 6. Pressure Rise as a Function of Initial Pressure
(pressures in psia)

P Initial	Δ P	P Final	$\dfrac{P\ Final}{P\ Initial}$	$\dfrac{\Delta\ P}{P\ Initial}$
1	.1	1.1	1.1	.1
2	.4	2.4	1.2	.2
3	1.7	4.7	1.6	.6
4	6	10	2.5	1.5
4.8	10	14.8	3.1	2.1

The strong dependence of pressure rise on initial pressure shows the increase in severity of the cool flame at lower altitudes and the relative insignificant effects at high altitude. The pressure rise associated with

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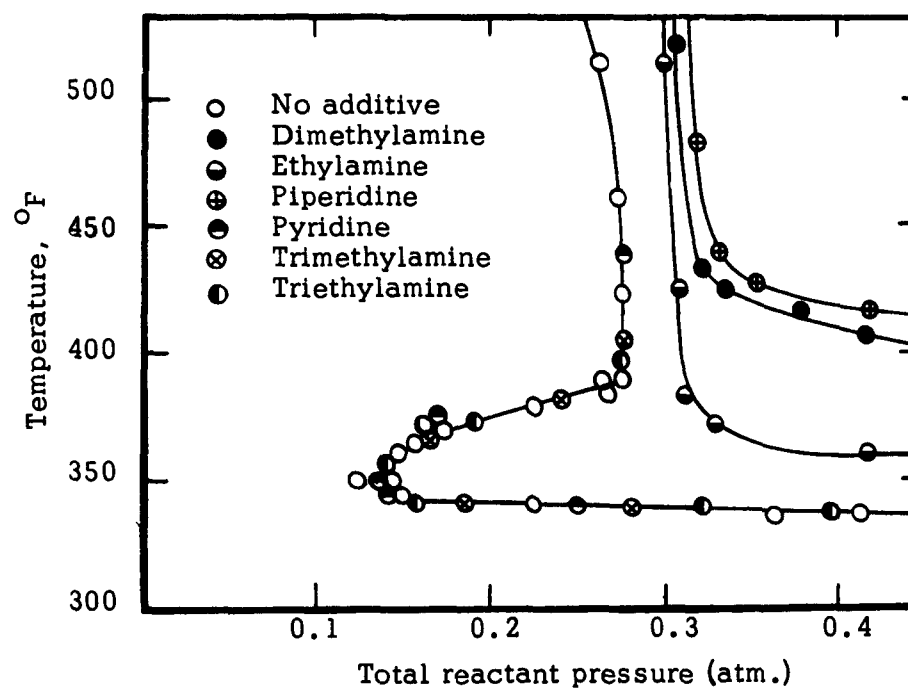
Figure 31. The Influence of Additives on the Explosion Limits
of a (1:3) Diethyl Ether – Oxygen Mixture
(Additive Added 4 Percent)

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flame propagation can be modified by the introduction of diluents as shown in Figure 32 from Ref 20. At any given altitude or initial pressure, the pressure rise decreases as the oxygen content of the gas decreases. To illustrate this effect the data are cross-plotted in Figure 33 which shows the variation of pressure rise with oxygen concentration at constant initial pressure (or altitude). At low oxygen concentrations a linear relationship between pressure rise and percent oxygen is observed, consistent with data obtained for other fuels. The sharp break in the curves of Figure 33 probably denote a transition from the cool flame region to the normal flame region and the associated higher pressure rises.

The data are replotted in Figure 34 in terms of pressure rise versus oxygen partial pressure. The single line appears to correlate the data for various pressures from 5 to 14.7 psia.

c. Normal Flames

Examination of Figure 25 shows another boundary between cool flames and oxidation and a region called normal flames. A normal flame is considered one in which the reactions proceed to thermodynamic equilibrium products and in which the full temperature rise is achieved. For lean and stoichiometric flames the products are CO_2 and H_2O and their dissociation products. It is evident from Figure 25 that normal flames can be achieved in two different ways.

The boundary between cool flames and normal flames indicates that cool flames can change to normal flames if the proper local conditions of temperature and pressure are achieved. This transformation involving two different kinds of flame has been called two-stage ignition. One may easily visualize the following set of circumstances. A mixture of fuel and air exists in a temperature and pressure environment which produces oxidation. The oxidation process can result in an increase in temperature or pressure or both until the conditions necessary for cool flame ignition are achieved. A cool flame, or in some cases several cool flames in succession, results and creates further changes in the temperature and pressure. When the critical conditions for a normal flame are reached, a normal flame is ignited and the flammable mixture is consumed.

An alternative single stage ignition to produce a normal flame can occur in the region in which the normal flame boundary adjoins the oxidation zone. In this region, one can visualize the oxidation process producing an increase in temperature until the critical conditions for ignition of a normal flame are achieved. This is the usual process considered when reference is made to ignition. Spontaneous combustion processes such as those associated with a pile of oily rags or a haystack involve this type of mechanism as do many gas phase systems.

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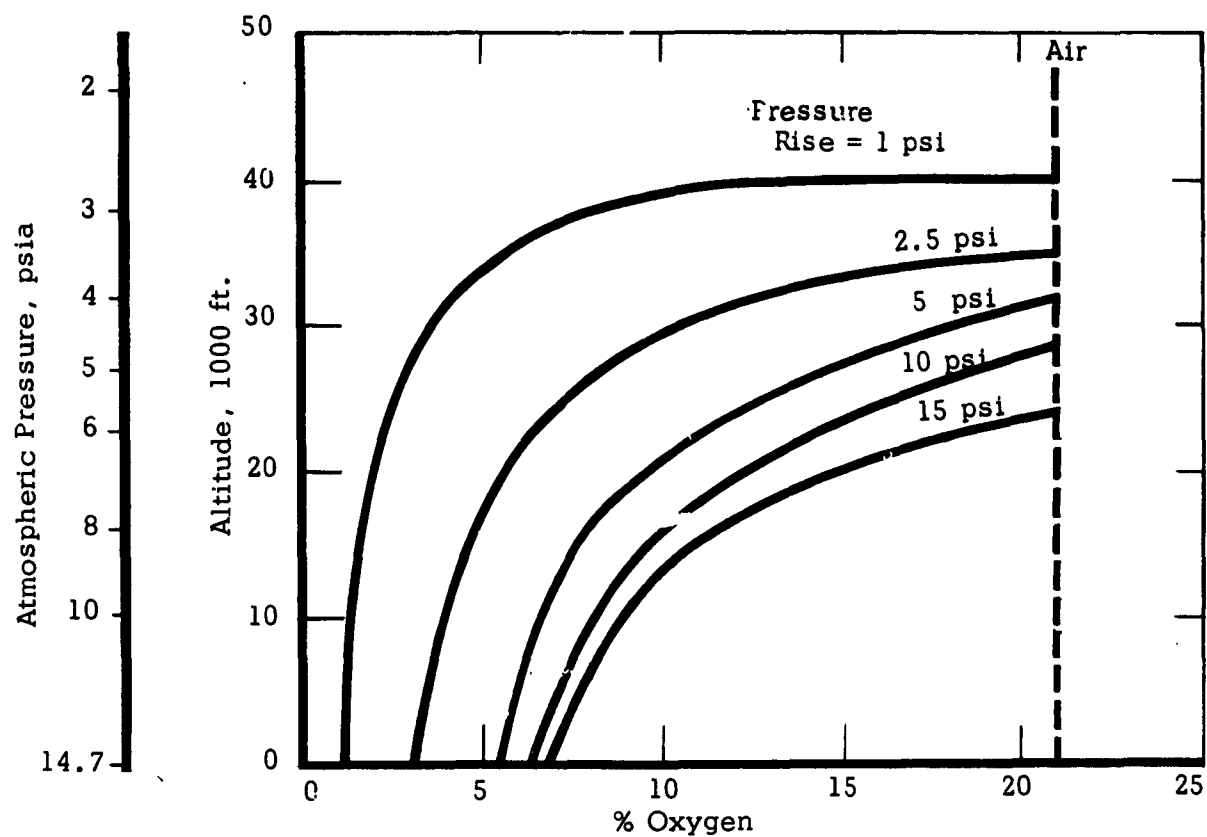
Note: Applies to the following diluents: Nitrogen, Carbon Dioxide, Water Vapor, and excess fuel.

Figure 32. Effect of Diluents on the Maximum Pressure Rise Obtained in Test Chamber

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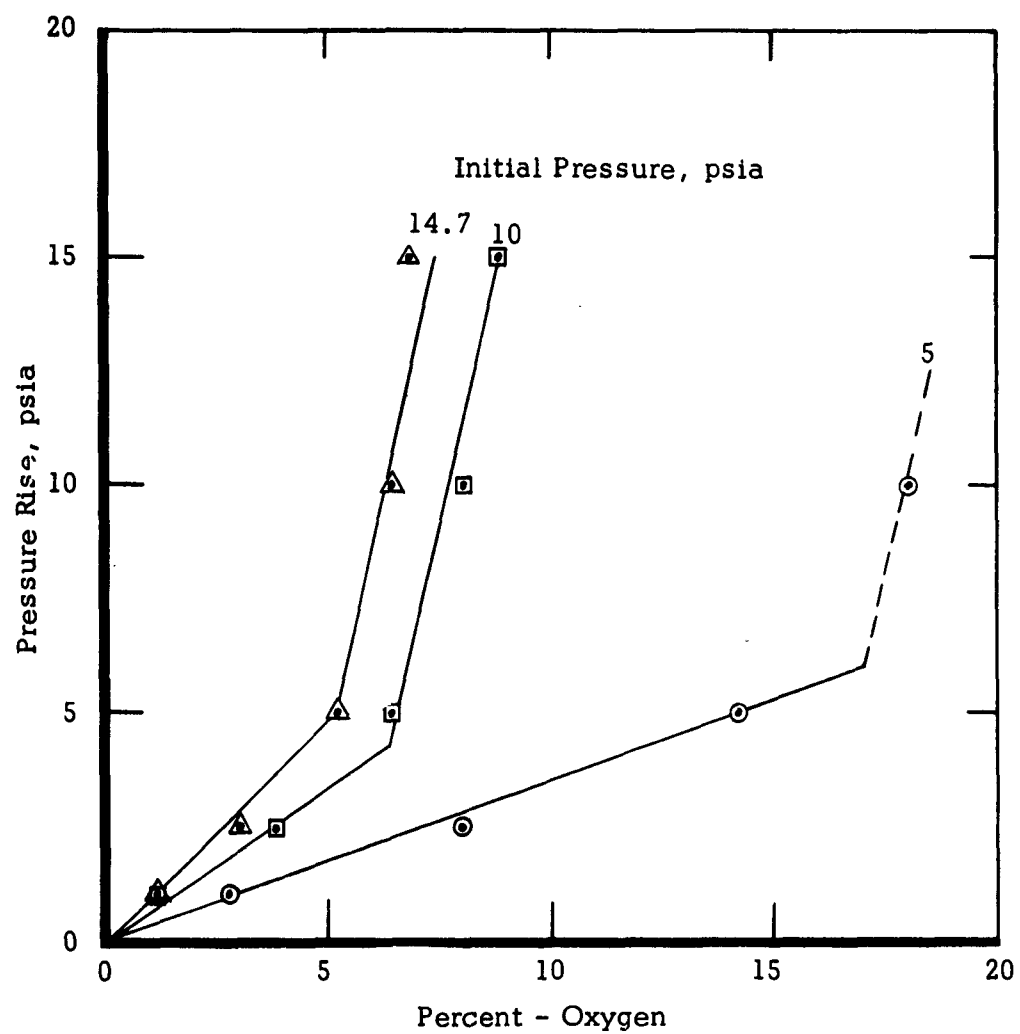
Figure 33. Change of Pressure Rise with Oxygen
Concentration

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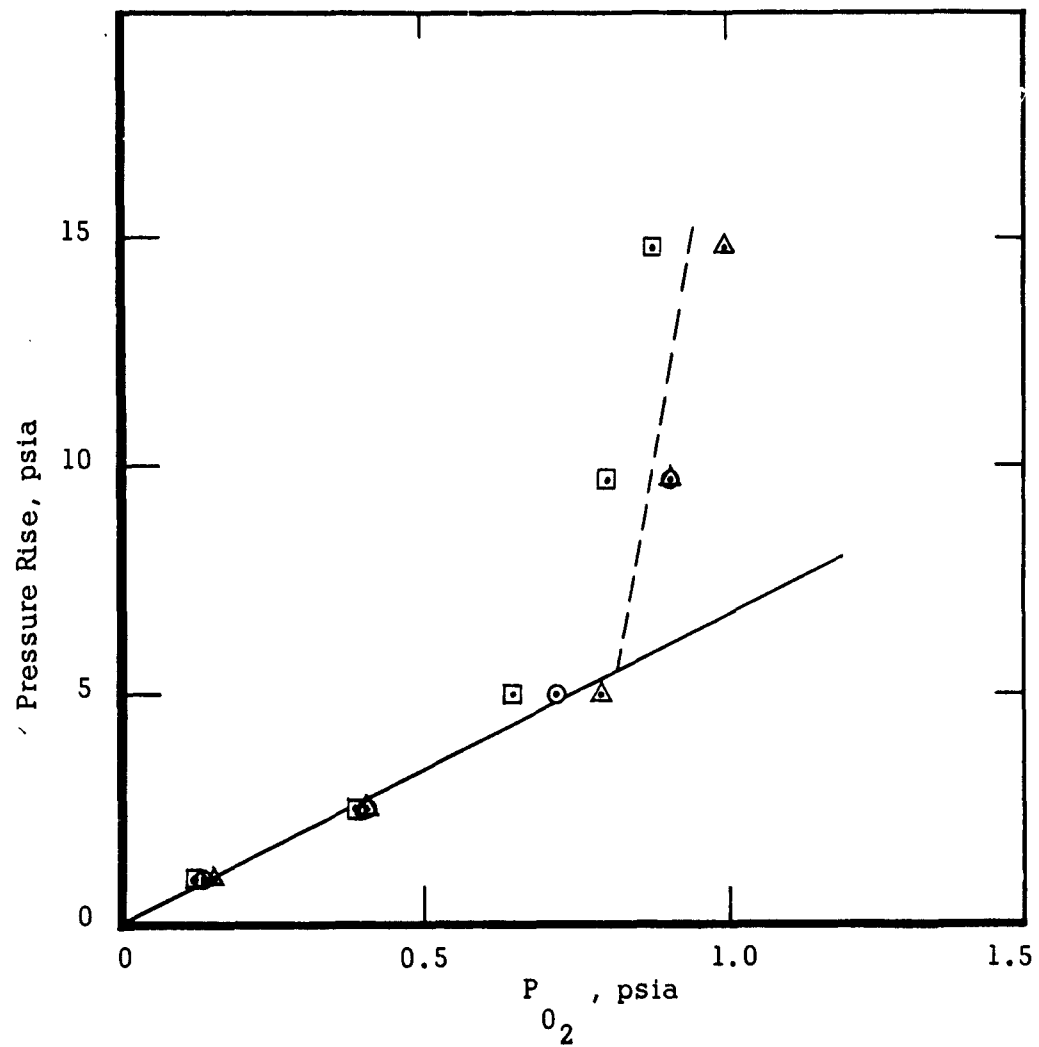
Figure 34. Variation of Cool Flame Pressure Rise with
Oxygen Partial Pressure

It is emphasized again that the oxidation process or the cool flame do not have to perform the entire task of achieving the conditions necessary for normal flame ignition if external environmental changes also occur. For example, it is generally immaterial how the pressure increase occurred that led to ignition. The necessary pressure rise may well have been a combined effect of an oxidation reaction and a change in ambient pressure level such as would occur during descent of an aircraft with a vented tank.

The normal flame, because of the high temperature and pressure rise associated with it, represents the principal hazard. The following discussion reviews some of the data, variables and concepts associated with the normal ignition process. The data on ignition has often been obtained under conditions where the nature of the flame cannot be observed and in some cases the ignition temperatures quoted may refer to cool flames. In any event, the reported ignition data represent a first estimate concerning the likelihood that ignition can occur.

Unfortunately, the many variables in ignition phenomena, some of which are not easily controlled nor clearly understood, create a dependence of the results on the experimental technique employed. These techniques will be described as a part of the ignition discussion.

One of the most widely used thermal ignition tests consists of dropping a small quantity of liquid fuel into an open container heated to some specific temperature. The container initially contains air. Ignition temperature is defined as the lowest temperature of the container or a bath surrounding the container at which a visible or audible evidence of a flame or explosion is observed. It is usually assumed that ignition will occur prior to some arbitrary time interval, usually several minutes. The ASTM autogenous ignition test as well as a number of modifications of this procedure, often called spontaneous ignition tests, are typical of the procedure just described.

Tests of this type generally give the lowest ignition temperatures reported. The experimental conditions correspond to the deposition of a relatively small quantity of liquid fuel on a heated surface in some sheltered region. The measured temperature for ignition is influenced by a number of factors which are discussed in the following sections.

It is possible to compare differences in the ignition temperature of various types of flammable liquids using the specific experimental conditions outlined above. Reasonable agreement is obtained by various investigators using such methods although some variations are observed and often not easily explained.

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Spontaneous ignition temperatures for a large number of pure hydrocarbons and some commercial fluids are reported in Ref 24. These have been reproduced in Table 7. A more recent compilation is presented in Table 7 from Ref 25. Additional data from Ref 26 are also presented in Table 7 for comparison. These data were obtained by essentially the same method, although differences in temperature distribution, method of injection of the liquid and the observer were present to a small degree. Variations of the order of 50^OF can be found for some compounds while others are much closer. Impurities might possibly account for some or all of the differences. If this is the case, then an uncertainty must always exist in such ignition temperature data since most of the compounds were of fairly high purity. Such effects due to impurities would tend to be random in nature and could account for the lack of a consistent trend among the measured values.

Some regularity does exist in the data, however, since the data of Ref 25 tend to be lower on the average. Comparison of relative values is facilitated by examining ratios or differences to some reference compound. Table 8 presents a comparison on the basis of ratios to n-pentane chosen as 1.00. Pentane was selected since there was fairly close agreement among the investigators. Table 9 presents the same data in terms of differences. Neither the ratios nor differences show a regularity between investigators.

The real problem is to select the proper value to use in evaluation of an ignition hazard. The safest choice, of course, is to use the lowest value. There is no assurance, however, that this value better fits the conditions involved in the hazard study nor that a future investigator will not find an even lower value. Nevertheless, for purposes of convenience the lowest values found in this study have been tabulated in Table 7 without regard to differences in technique or purity of material which often is not specified.

Most of the work using the ASTM type of apparatus has been performed in glass containers in open air. Some variations of container material and pressure have been made, however. No data on the effect of initial fuel temperature on spontaneous ignition temperature have been found to this time. At first estimate, one might suppose that the initial fuel temperature would have no effect since the fuel becomes heated by the vessel in which it is placed. It will be shown that this result is by no means obvious and that the spontaneous ignition temperature could possibly be higher for some fuels and lower for others as a result of increases in initial temperature.

The effect of pressure on spontaneous ignition temperature has been studied in variations of the ASTM autogenous ignition apparatus. Data for JP-4 fuel below 1 atmosphere from Ref 25 and above 1 atmosphere from Ref 27 are plotted in Figure 35. In the range from 0.2 atm to 2.5 atm there

Table 7. Spontaneous Ignition Temperatures

Fuel	S.I.T. °F			
	Ref.24	Ref.25	Ref.26	Lowest
Propane	940		920	92C
Butane	807	761	766	761
Pentane	544	549	554	544
Hexane	501	453	478	501
Heptane	477	433	446	433
Octane	464	428	424	424
Nonane	453	403	545	403
Decane	449	406	482	406
Hexadecane	446	401	455	401
Iso octane	837	784		784
Av. Gas 100/130	844	824	804	804
Low volatility Av. Gas (49% arom.)	943	–	–	943
Low volatility Av. Gas (20% arom.)	900	–	–	900
Kerosene	480	442	489	442
SAE #10 Oil	720	–	–	720
SAE #60 Oil	770	–	–	770
JP-3		460	–	460
JP-4		468	–	468
JP-5				450 *
JP-6				440 *

* from Ref 28

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Table 8. Ratios of S.I.T. to Pentane

Propane	1.73		1.661
Butane	1.485	1.386	1.384
Pentane	1.00	1.00	1.00
Hexane	.922	.826	.863
Heptane	.878	.789	.806
Octane	.853	.780	.766
Nonane	.830	.734	.984
Decane	.826	.740	.870
Hexadecane	.820	.730	.822

Table 9. Differences of S.I.T. from Pentane, $^{\circ}F$

Propane	-396		-366
Butane	-263	-212	-212
Pentane	0	0	0
Hexane	43	96	76
Heptane	67	116	108
Octane	80	121	130
Nonane	91	146	9
Decane	95	143	72
Hexadecane	98	148	9

78
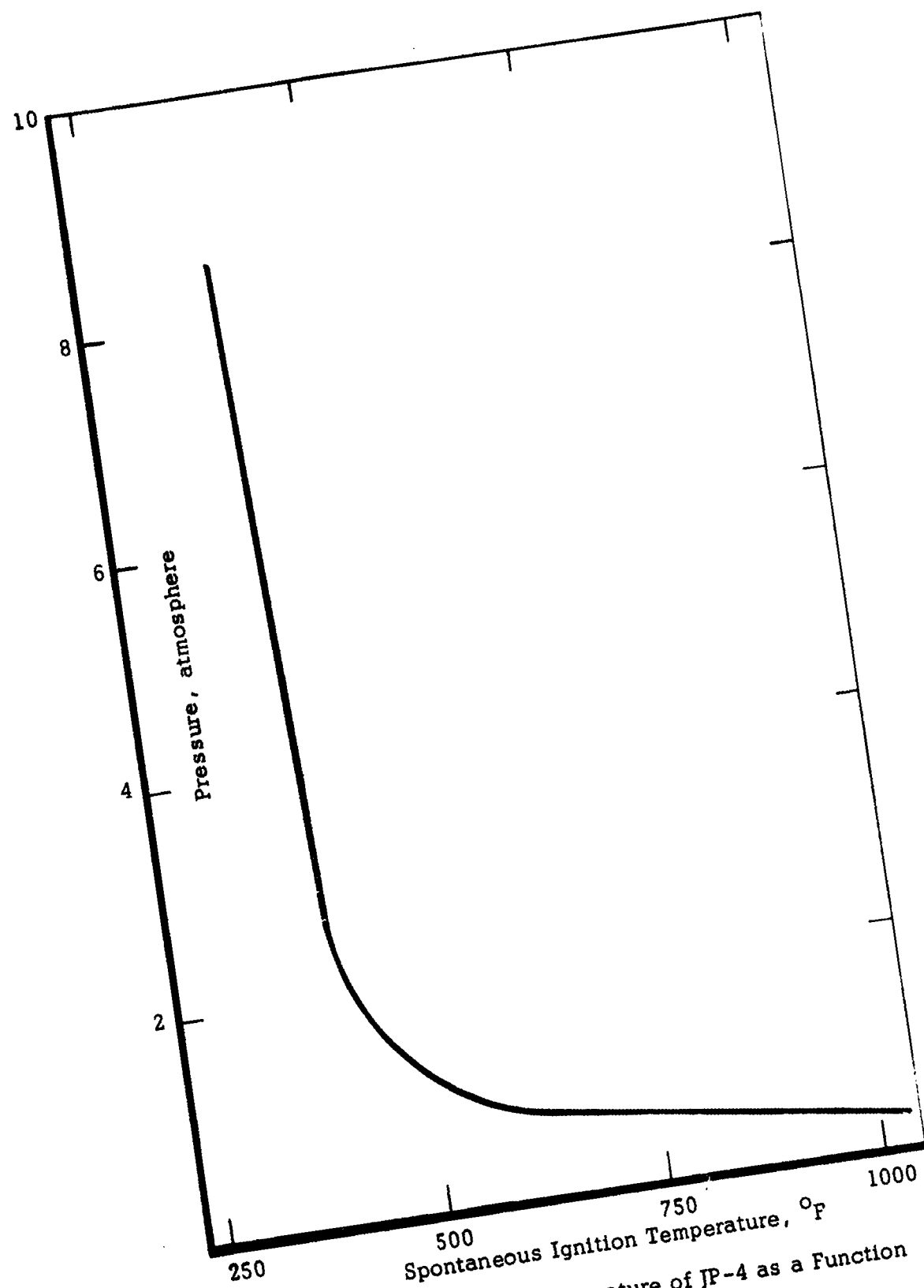
Figure 35. Spontaneous Ignition Temperature of JP-4 as a Function of Pressure

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is a rapid decrease in spontaneous ignition temperature as pressure increases. There is apparently little difference between 2.5 and 9 atmospheres. Tabulated data for JP-4 and JP-5 above 1 atmosphere are given in Table 10 below. Additional data are presented in Figure 36 from Ref 28.

Table 10. Variation of Ignition Temperature
with Pressure (Ref 27)

Pressure atm.	Ignition Temperature $^{\circ}F$	
	JP-4	JP-5
1	484	477
5	376	415
9	378	408

Data for several pure hydrocarbons and commercial fuels are tabulated in Table 11 (Ref 25).

Table 11. Ignition Temperatures of Commercial
Fluids at 2 Pressures

Combustible	Pressure	
	1/2 atm.	1 atm.
JP-4	831°F	468°F
JP-3	840	460
JP-1	864	442
Av. Gas 100/130	1027	824
Av. Gas 115/145	1063	880
n-hexane	927	453
n-octane	869	428
n-decane	856	406
Hydraulic Fluid AN-0-366	838	437

80
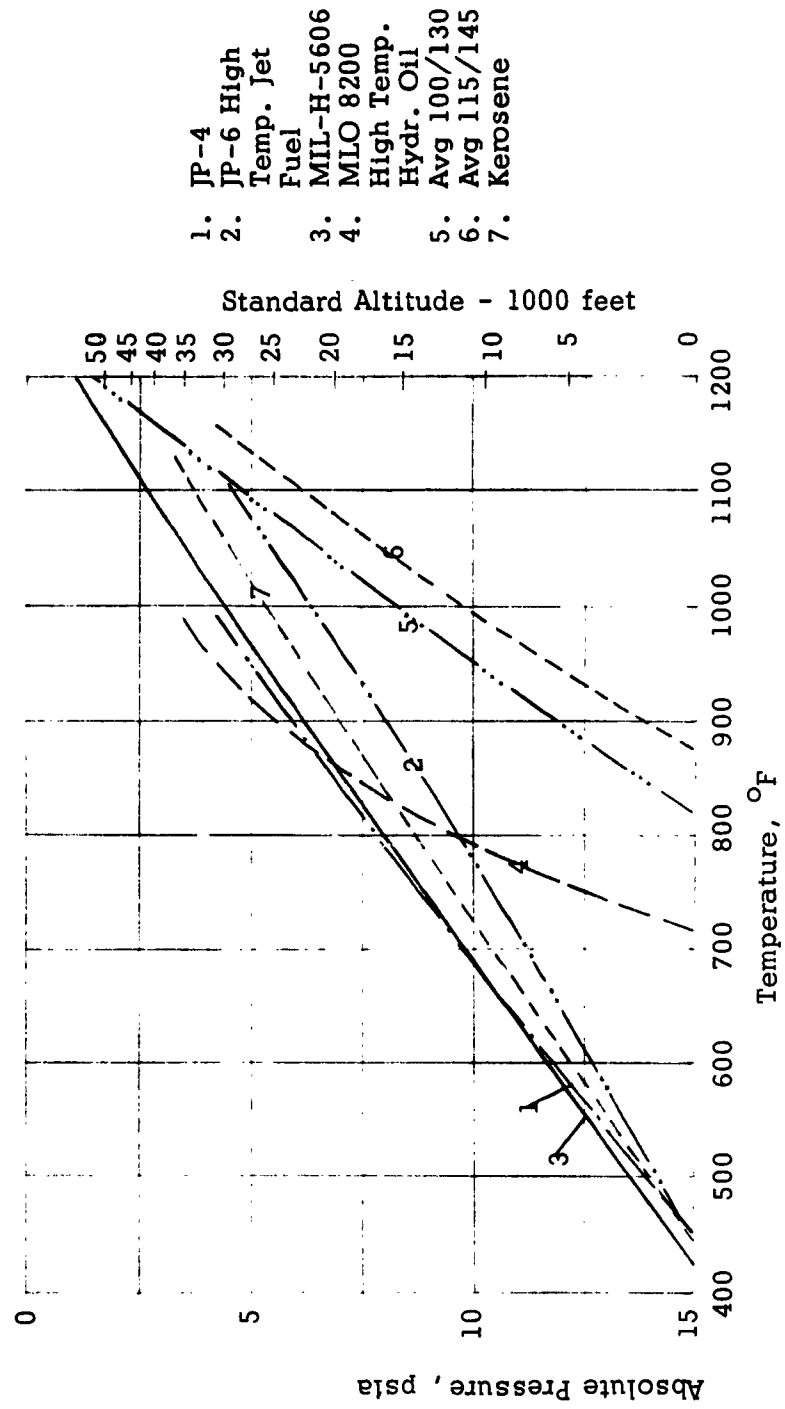
Figure 36. Variation of the Minimum Spontaneous Ignition Temperature with Pressure

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The low pressure ignition temperature variations for JP-4, JP-5, and JP-6 also can be found in Figure 29. The boundary between cool flames or no ignition and normal flames corresponds to the ignition temperature discussed in this section. Comparison of the data for JP-4 in Figure 35 with similar data in Figure 29 shows that the change of ignition temperature with pressure follows essentially the same type of curve but that the data of Figure 29 show generally lower ignition temperatures.

The ignition temperature is also dependent on the oxygen content of the atmosphere to which the fuel is added. Some ignition work with the ASTM type apparatus has been done in pure oxygen. In most cases the use of an oxygen atmosphere instead of air causes a slight reduction in spontaneous ignition temperature. In a few cases which cannot be explained there is an appreciable reduction in an oxygen atmosphere, but such cases are fairly rare. Some data from Ref 26 are presented in Table 12 to illustrate the effect of oxygen.

Table 12. Comparison of Ignition Temperature
in Air and Pure Oxygen

Fuel	S.I.T. $^{\circ}F$	
	Air	O_2
Butane	766	542
Heptane	446	417
Octane	424	406
Pentane	554	496
Propane	920	874
2, 2, 4 - Trimethyl- Pentane	813	542

In general one can assume that the spontaneous ignition temperature will increase as the oxygen content decreases but the magnitude of the change is not predictable on the basis of present knowledge. In the absence of definitive data it would appear from the limited data of Table 12 that large diluent concentrations would be required to markedly increase the spontaneous ignition temperature of paraffin type fuels unless the diluent had a pronounced chemical effect. Such a conclusion, however, is based more on intuition than on fact.

The spontaneous ignition temperatures of petroleum base oils are reported in Ref 29 using a modification of the ASTM method known as the Sortman, Beatty and Heron method (Ref 30). This modification of the ASTM method utilizes a slow flow of air into the ignition flask. The results are generally a little higher than the spontaneous ignition temperatures determined by the usual static air method. This method is discussed again in connection with the effect of additives on S.I.T. The results for petroleum oils are summarized below:

Table 13. Comparison of Ignition Temperature of Petroleum Base Oils with Pure Hydrocarbons

Fluid	S.I.T. ^{O}F
Benzene	1295
n-hexadecane	465
Hydraulic oil O.S. 1113	505
Lubricating oil N.S. 2135	685

Chlorination of hydrocarbons produces compounds of relatively high S.I.T. as shown in Table 14 (Ref 29).

Table 14. Ignition Temperature of Chlorinated Hydrocarbons

Fluid	S.I.T. ^{O}F
1, 2, 4 Trichloro benzene	1000
Trichloro cumene	1000
Trichloro diphenyl	1230
Tetrachloro diphenyl	1300
Polychloro ethylene	1000
Hexa chloro butadiene	1000

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Silicone fluids are widely considered at the present time for high temperature oils and hydraulic fluids. Typical data for a variety of silicones are given in Table 15 (Ref 29).

Table 15. Ignition Temperatures of Silicone Oils

Fluid		S.I.T. ^{O}F
Polymethylsiloxane DC 190		860
	DC 500	860-920
	GE(0-73)	890
	DC 200	890-910
	GE (A-199B)	890
Polyethylsiloxane	DC-400	540-610
	DC 400B	505-590
Poly (methyl, phenyl) siloxane	DC 700	940-990

The methyl and phenyl siloxanes have spontaneous ignition temperatures of the order of 800-900°F while the ethyl siloxanes compare closely with hydrocarbon oils in the 500-600°F range.

Another class of polymers, poly alkylene glycol derivatives, which are also of interest as oils and hydraulic fluids have spontaneous ignition temperatures of the order of 700°F (Ref 29).

Only a little work has been done on the effect of additives on spontaneous ignition temperature. Tetra-ethyl lead has been the principal additive studied. In general a comparison between leaded and unleaded fuels shows a significant increase in ignition temperature due to the addition of tetra-ethyl lead.

Apparently the nature of the surface can affect the measured ignition temperature. It is part of the ASTM procedure in fact that the pyrex glass surface be conditioned by repeated ignitions until reproducible results are

obtained. There appears to be a difference between a fresh pyrex surface and a conditioned surface. The nature of the surface effect has not received much investigation so that the mechanism by which the surface influences the ignition temperature is not known. Observations of the ignition process indicate that ignition occurs in the vapor space removed from the surface. It is difficult, then, to attribute to the surface catalytic effects on the ignition reactions. The surface nature may influence thermal decomposition of the fuel as well as the physical processes of heat transfer and vaporization. The observed surface effects are probably combinations of a variety of processes, the nature of the influence depending upon the nature of the surface.

A comparison of ignition temperatures in containers of different materials is given in Table 16 (Ref 31).

Table 16. Effect of Cup Material on Ignition Temperature

| Fuel | S.I.T. ^{O}F | | | |
	Pyrex	Copper	Low Carbon Steel	Chromium
n-Hexane	479	510	516	513
n-Heptane	452	481	484	483
Isobutyl alcohol	825	861	902	862
Gasoline	497	534	550	559

Platinum also shows a higher ignition temperature than pyrex (Ref 32). Pyrex seems to be the optimum surface for ignition, giving the lowest ignition temperatures of the materials tested. One possible explanation is that the lower conductivity of pyrex compared to the metals slows down heat transfer from the reacting mixture out of the container. The lower heat transfer rate to the liquid may not be significant if the heat capacity of the container is sufficient to rapidly heat the liquid fuel without a noticeable drop in temperature. The consistently lower values for copper are not consistent with this explanation, however, although the difference between copper and the other metals is less than the difference between the metals and glass. Nevertheless, the data suggest that heat transfer alone is not a sufficient explanation.

Surface geometry can also affect the measured ignition temperature. A comparison between a flat plate and a tube is presented in Table 17 (Ref 33).

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Table 17. Effect of Geometry on Ignition Temperature

Fuel	Ignition Temp. °F	
	Tube	Plate
Gasoline unleaded	473	1238
100-octane Av. Gas leaded	734	1238
Kerosene	417	1202
Hydraulic Fluid	455	752
Oil	572	806

Producing a sheltered zone apparently permits much lower ignition temperatures than does a flat plate. The rapid boil-off of the fuel and dilution with air is undoubtedly the principal reason. The difference between the tube and the plate is less for a low volatility oil than for a high volatility gasoline which is also consistent with the effect of boil-off and dilution on ignition temperature. The marked difference between the leaded and unleaded gasoline in the tube is consistent with the effect of tetra ethyl lead cited previously.

One modification of the ASTM static cup type of ignition temperature measurement introduces a relatively low flow of air into the cup. The air flow certainly must influence local fuel-air ratios within the cup and possibly local temperatures as well. Nevertheless, for fairly low flow rates, the ignition temperatures measured in this manner often do not differ greatly from those obtained with no air flow. As an example of the kind of agreement which has been obtained, the spontaneous ignition temperature of n-heptane in a steel cup with no air flow is reported as 484°F (Ref 31) and as 490°F with an air flow of 50 cc./min. (Ref 30).

The effect of flowing air, generally, is to increase the spontaneous ignition temperature. At an air flow rate of 54 cc/min an ignition temperature of 498°F is reported while for 330 cc/min the value is 806°F for heptane (Ref 32). It is evident that even a fairly mild air flow can have a large influence on the ignition temperature. In the experiment cited, the flowing air is cold, normal ambient temperature. Heated air, same temperature as the cup, would probably have less effect although it is possible that the dilution of fuel vapor is more important. If the major effect is dilution, then the air temperature is less important. On the other hand, if residence time

near the hot surface is the critical factor then the air temperature would be important. A better understanding of the effect of air flow on spontaneous ignition temperature is needed.

Experiments using flowing air in a cup type ignition test have been used to demonstrate the effect of tetra-ethyl lead on ignition temperature. In all cases (see Ref 32) tetra-ethyl lead increased the ignition temperature, sometimes by increments as high as 482°F. Apparently, tetra-ethyl lead was more effective in the experiments involving low air flow than in those involving higher air flows.

Another type of ignition experiment utilizes a closed bomb. Generally the ignition involves a vapor phase mixture of fuel and air. Some typical data utilizing the closed bomb method are illustrated in Figure 37 (Ref 32). Several significant indications may be drawn from the figure and from a comparison of the data with those obtained in other experiments.

Except for methane, there is a trend toward decreasing ignition temperature with increasing fuel content in the mixture. One would expect that the liquid injection characteristic of the ASTM type ignition test would give rich mixtures. The curves tend to flatten out, however, so that it is unlikely that the presence of rich mixtures in the ASTM type cup test is a complete explanation for the difference. A few comparisons may be of interest. The lowest data points from Figure 37 are used for the comparisons.

A comparison of the data of Figure 37 with similar data from open cup tests is shown in Table 18.

Table 18. Comparison of Bomb and Open Cup Data

Fuel	Spontaneous Ignition Temp. °F	
	Bomb	Open Cup
Methane	1265	–
Ethane	995	959
Propane	960	920
n–Butane	925	766
n–Pentane	890	554

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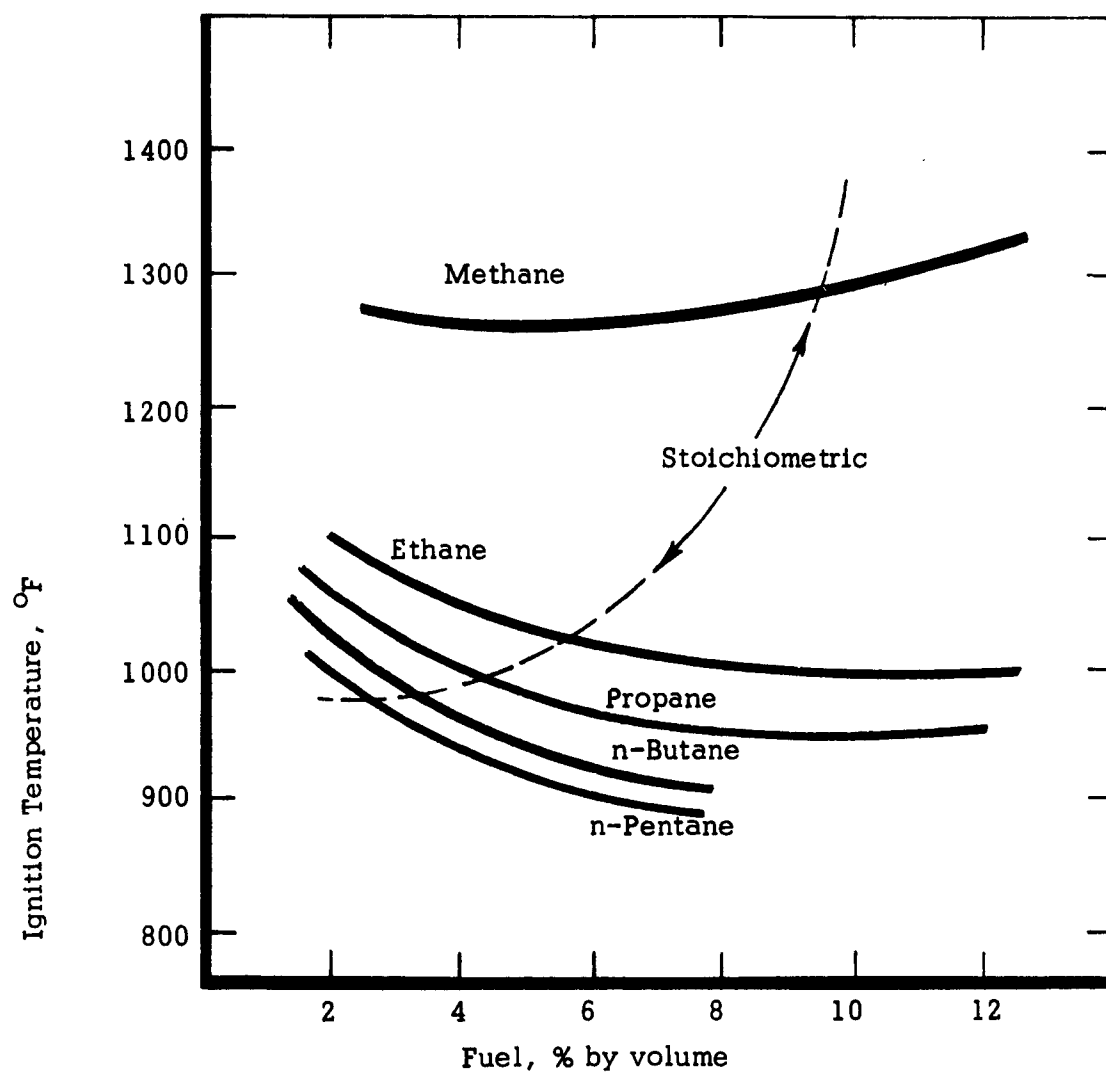
Figure 37. Variation of S.I.T. with Mixture Composition
(Closed Bomb)

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Reasonably good agreement is found between the bomb and open cup for very volatile fluids such as ethane and propane, while wide differences are noted for butane and pentane. Fuel volatility obviously is important, but the exact nature of the volatility effect in terms of an ignition mechanism is not obvious. Another comparison is also of interest. The ignition temperature for pentane in the cup-type apparatus with air flow (330 cc/min) is 959°F (Ref 32) which compares more closely with the bomb ignition temperature for low fuel content (see Figure 37).

Another comparison is also of interest. In Table 19 (Ref 32) the spontaneous ignition temperature for gasoline obtained by the cup method with and without flow and the bomb method with liquid injection are compared:

Table 19. Spontaneous Ignition Temperatures for Liquid
Injection of Gasoline

Method	Spontaneous Ignition Temp. °F
Static Cup	824-880
Cup - 50 cc/min flow	830
Cup - 330 cc/min flow	860
Bomb	460

The low temperature obtained in the bomb experiment shown in Table 19 is difficult to explain. Variations in the nature of the gasoline could account for part of the difference, but additional experimental work is needed to understand the differences between the various techniques.

A considerable amount of work using a closed static bomb as the test container but employing liquid injection into the heated air space has been reported by Setchkin (Ref 34). These experiments are of interest since they represent a version of the ASTM type test under somewhat better controlled experimental conditions. Some representative data using this technique are compared with the static open cup method typified by ASTM methods in Table 20.

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Table 20. Comparison of Ignition Temperature in Static
Bomb with Other Methods

Fuel	Spontaneous Ignition Temp. $^\circ$F		
	Setchkin (1 liter flask)	Open Cup	Vapor Bomb
n-pentane	496	544	888
n-heptane	433	477	806
Gasoline (65 octane)	478		995
Gasoline (73 octane)	496	570	
Kerosene	441	480	
Motor Oil	664	720-770	
Benzene	1038	1097	1328

Although the ignition temperatures determined in the Setchkin apparatus are lower than those reported in Ref 24 for a modified ASTM apparatus, the differences are not large and are of a similar magnitude to the differences between different investigators using the open cup method. Compare these results with the data in column 3 of Table 20 for vapor-air mixture injection into a closed bomb and it is evident that the experiments no longer compare favorably. The difference must be attributed to one of two factors or a combination. The injection of a liquid could result in liquid phase cracking reactions which create a more easily ignited gaseous mixture or the liquid on evaporation could produce rich fuel zones which are more easily ignited.

The reduction in ignition temperature due to enrichment of the mixture with fuel has been demonstrated and is discussed in detail in a later section of this report. These differences, however, do not account for the wide variations between liquid and vapor injection so that the presence of a liquid phase must be a part of the answer. This conclusion was also indicated in the discussion of the data in Table 18.

The volume of the bomb has an effect on the observed ignition temperature. In general, the larger the bomb volume the lower will be the ignition temperature until a minimum value is obtained. Presumably this effect of volume is associated with heat losses from the bomb, these losses decreasing

as the volume increases. If it is assumed that ignition occurs when the chemical reactions of the flammable with air generate heat at a faster rate than heat is lost from the system, then the decrease in ignition temperature with increasing volume is consistent with this concept. Even the occurrence of a minimum temperature is reasonable since the rate of loss also levels off as the bomb volume increases.

Some data obtained in the Setchkin apparatus are plotted in Figure 38 to illustrate the effect of bomb volume on spontaneous ignition temperature. The same data for ignition temperature are plotted versus volume to surface ratio in Figure 39. Since heat generation rate should be proportional to the volume and heat loss rate to the surface area of the container one would expect a decrease in ignition temperature with increasing V/S as shown. The important factor to be noted here is that the effect is small except for very small volumes so that one cannot expect a large influence of free volume in most practical situations. The dimensions which produce large increases in ignition temperature are within an order of magnitude quenching distances which will be discussed in a later section.

The effect of quantity of fuel in a given quantity of air on ignition temperature has been suggested as one of the differences between ignition temperatures measured by the introduction of liquid fuel and those measured by the introduction of a vapor fuel-air mixture. While somewhat different trends may be found with different types of flammable materials, in general and for hydrocarbons in particular, the ignition temperature decreases with increasing fuel-air ratio until fairly large values of fuel-air ratio are reached. The general nature of the variation is illustrated in Figure 40 with data obtained in the Setchkin apparatus.

The minimum in the curve corresponds very roughly to more than ten times the stoichiometric fuel-air ratio by weight if one assumes complete vaporization of the fuel.

Another type of spontaneous ignition experiment involves the use of a flowing stream of fuel and air in a heated pipe. Various modifications of such experiments exist which differ principally in the manner in which the fuel and air are pre-heated and mixed. The chief advantage of this type of experiment is that it permits better control of the experimental variables and usually an opportunity to measure such aspects as ignition delays and effects of initial variables on both ignition temperature and ignition delay. The method is not without its problems, however, since the measured ignition temperatures often depend on the nature of the heating and mixing processes, flow parameters and methods of observation. The flow methods are usually restricted to fairly short ignition delays which makes comparison difficult with the relatively long delays associated with the static methods. A discussion of ignition delays will be given in a later section.

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Figure 38. Effect of Bomb Volume on Spontaneous Ignition Temperature

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Figure 39. Variation of Spontaneous Ignition Temperature with V/S Ratio

Figure 40. Effect of Charge Volume on Spontaneous
Ignition Temperature

The general concept of thermal ignition which has been used in the preceding discussions associates the ignition phenomenon with the situation that the heat generation rates exceed the heat loss rates. A critical condition may then be supposed to exist when these rates are equal. For a given experimental environment, therefore, ignition may be considered to occur when a critical reaction rate has occurred.

The rate of a chemical reaction may be expressed in the form of the Arrhenius expression as

$$R = Ae^{-E/RT} f(c) \qquad (27)$$

where
A = pre-exponential factor
E = activation energy
R = gas constant
T = temperature
f(c) = function of concentration

The reciprocal of such a critical rate may be considered as a reaction frequency or, of a critical extent of reaction is assumed always to be involved, as a time lag. For practical purposes, without considering a rigorous treatment of the problem, one may write for the ignition delay:

$$\mathcal{T} = A^1 e^{E/RT} \qquad (28)$$

where
$$A^1 = \left[Af(c) \right]^{-1} \qquad (29)$$
$$\mathcal{T} = \text{time lag for ignition}$$

while the relationship between time lag and temperature has been presented rather than derived, derivations of similar expressions can be found in the literature (Ref 35, e.g.). For the purposes of this report, the important point is that the time lag is an exponential function of the temperature and, conversely, the temperature of ignition can be expressed as a logarithmic function of the time lag.

$$\frac{1}{T} = \frac{R}{E} \log Af(c) \mathcal{T} \qquad (30)$$

There is ample evidence in the literature that a plot of $\log \mathcal{T}$ vs. $1/T$ does, in fact, give a straight line over a reasonable range of values. The value of E to be used in the equation varies with the specific fuel and also with the temperature so that the best use of the relationship requires an empirical determination of E. In the absence of experimental data a value of E of the order of 40,000 kcal/mole is often a reasonable estimate for hydrocarbons.

The relationship between ignition delay and temperature can be approximated by taking the first two terms in the expansion of e^x where

$$e^x = 1 + x + \frac{x^2}{2!} + \ldots$$ (31)

so that

$$\mathcal{T} = A^1 \left(1 + \frac{E}{RT}\right)$$ (32)

and, in a similar manner

$$T = \left(\frac{E}{R}\right) \left(\frac{\mathcal{T}}{\mathcal{T} - 1}\right) + \text{constant}$$ (33)

The variation of T with   can also be written in the form

$$T = \left(\frac{E}{R}\right) \left(\frac{1}{1 - 1/\mathcal{T}}\right) + \text{constant}$$ (34)

In the limit as $\mathcal{T} \rightarrow$ infinity

$$T = \frac{E}{R} + \text{constant}$$ (35)

which is consistent with the concept of a minimum ignition temperature for very long time lags.

Typical variations of ignition delay with temperature are illustrated in Figure 41 (Ref 36) for the high temperature region and in Figure 42 (Ref 34) for the low temperature region.

Similar relationships may be written for the dependence of ignition delay on pressure. If one writes the concentration dependence as a pressure dependence since

$$C = \frac{P}{RT}$$ (36)

for a perfect gas, the dependence of $f(c)$ on pressure can be written as

$$f(c) \sim P^n$$ (37)

where n is related to the empirical reaction order. For a constant ignition temperature, one can relate the ignition delay to pressure according to the expression

96
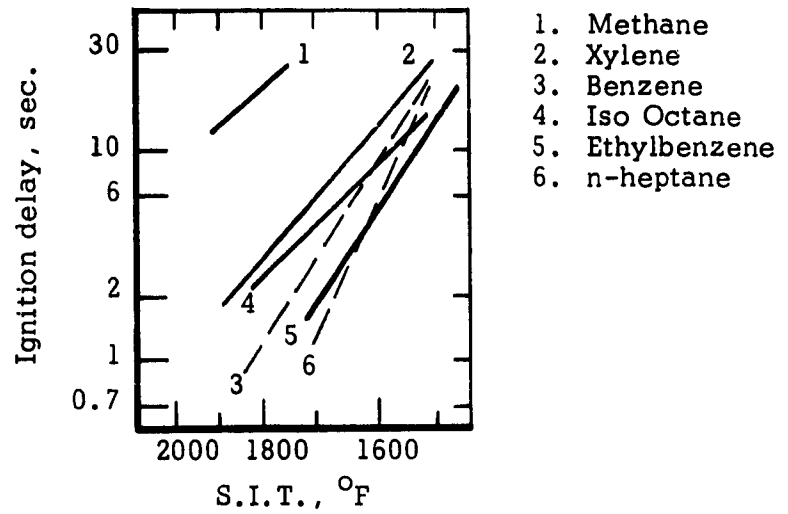
Figure 41. Variation of Ignition Delay with Temperature

1. Methane
2. Xylene
3. Benzene
4. Iso Octane
5. Ethylbenzene
6. n-heptane
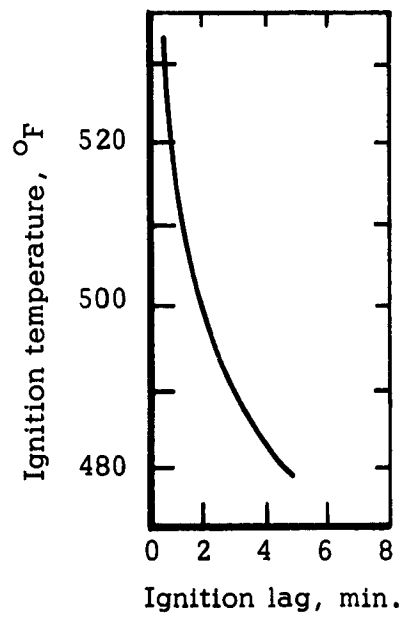
Figure 42. Ignition Lag versus Temperature for Gasoline

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$$\Upsilon = P^{-n} + \text{constant} \tag{38}$$

where n varies between 0.5 and 2.0 with a value of 1.5 serving as a reasonable estimate for hydrocarbon fuels such as kerosene (Ref 36).

For the case of very long delay times one can then relate ignition temperature to pressure according to a relationship of the form

$$\frac{1}{T} = \frac{R}{E} \ln P^n + \text{constant} \tag{39}$$

which shows T decreasing as P increases, in agreement with experimental data. The semi-logarithmic type of curve illustrated in Figure 43 also has the characteristic of levelling off at high values of P as indicated in the data cited previously and producing rapidly increasing values of T for low values of P.

The relationship of ignition temperature with pressure through the concentration dependence of reaction rate implies a similar relationship between ignition temperature and fuel-air ratio. For the situation where the fuel represents only a small part of the total mixture, if the function $f(c)$ is represented by

$$f(c) = \frac{1}{5} C_F C_A \tag{40}$$

then C_A is almost the total mixture for $C_F \quad C_A$ and as a gross approximation we can write

$$C_F \sim F/A \tag{41}$$

$$C_A \sim 1 \tag{42}$$

so that $f(c)$ becomes

$$f(c) \sim F/A \tag{43}$$

On this basis a plot of log F/A vs 1/T should be linear. Figure 44 shows such data from Ref 36 and a crude fit is obtained. An actual plot of F/A vs T should also show only a slight change of T for increasing F/A on one limit of the curve, consistent with the concept in the ASTM type experiment that gradually increasing the liquid fuel quantity has a minor effect on S.I.T. A similar trend was found in the Setchkin apparatus (Figure 40). Figure 45 shows the trend of F/A with T for the flowing gas in a tube experiment.
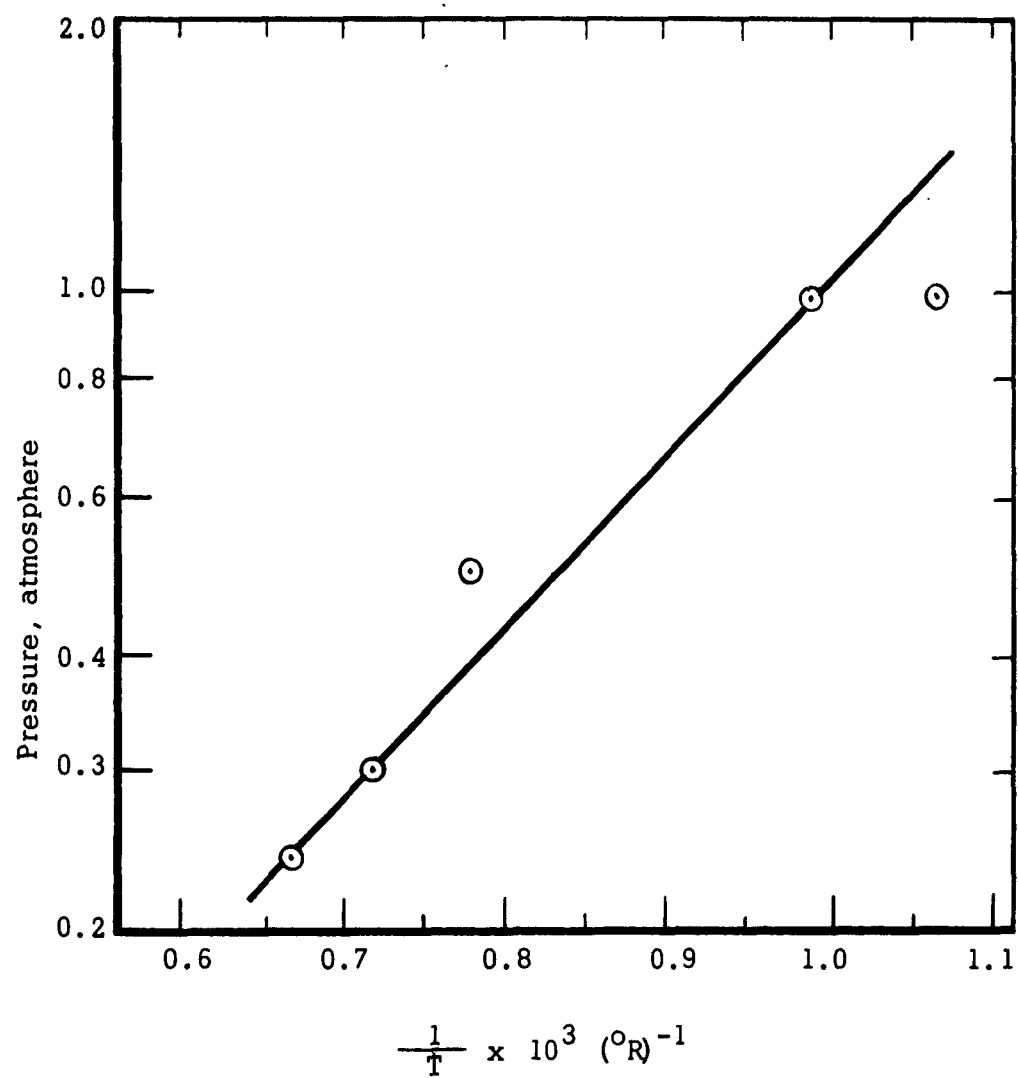
Figure 43. Variation of Ignition Temperature with Pressure
(log P vs 1/T)

99
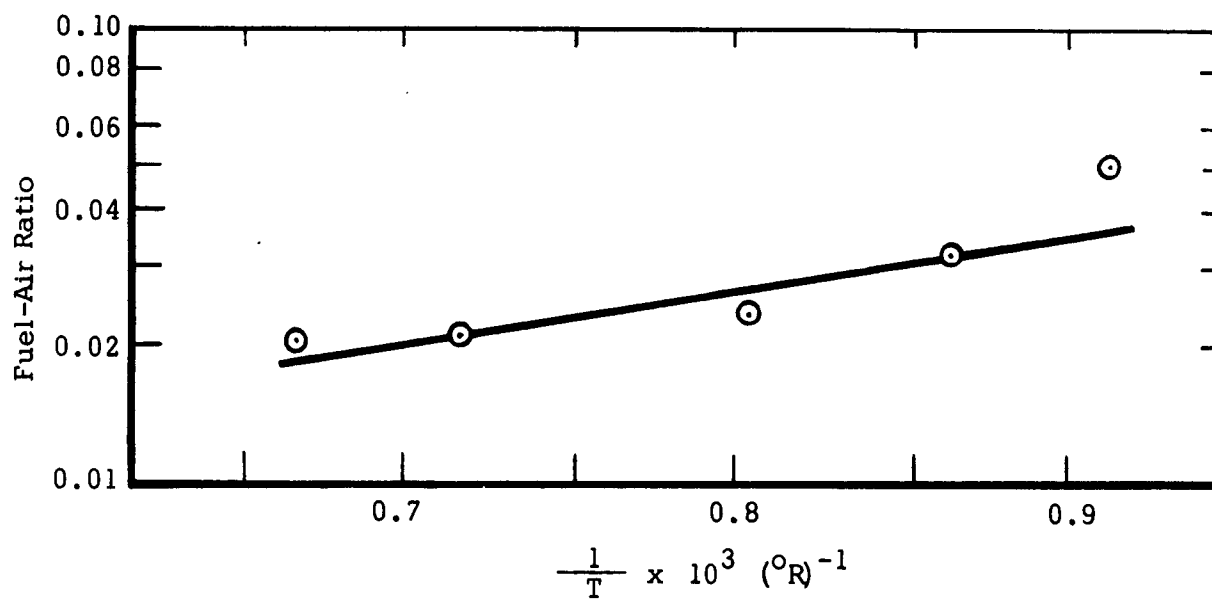
Figure 44. Variation of the Logarithmic of Fuel-Air Ratio with
the Reciprocal of the Ignition Temperature

100
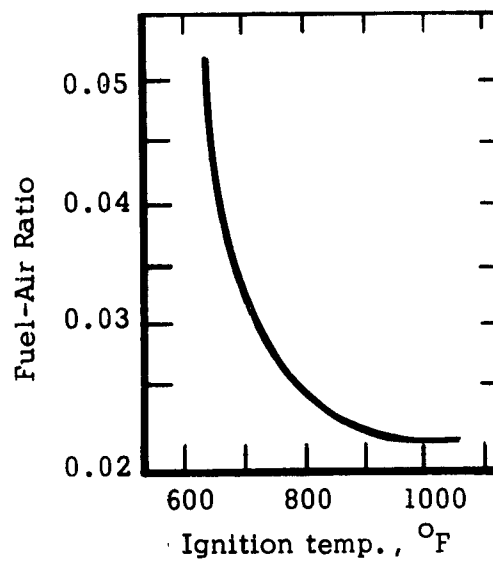
Figure 45. Variation of Ignition Temperature with Fuel-Air Ratio

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This discussion of ignition delay as related to ignition temperature has indicated the importance of the time parameter in the measurement and interpretation of ignition temperatures, as well as serving as a basis for relationships such as those involving ignition temperature and pressure.

The equations presented in the previous discussion can also be used to describe the effect of gas flow velocity on ignition temperature. Theoretically, the temperature at which the gases achieve a given reaction rate should be independent of gas flow velocity. In a given experiment, however, the wall temperature which produces the critical gas temperature is determined by a balance between heat generation and heat transfer. Since flow velocity affects the rate of heat transfer, the wall temperature required to produce ignition depends upon the flow velocity.

A rough empirical variation of ignition temperature with wall temperature can be derived by:

1. Use a heat generation term such as Equation (27).

2. Use a heat loss term of the form $q_L = h (T_c - T_w)$.   (44)

3. Let $h = h_0 + aU_s^m$ (45)

where h = heat transfer coefficient, overall

    h_0 = conduction heat transfer coefficient

    U_s = stream velocity

    a, m = empirical constants

Such an equation introduces the effect of flow velocity in terms of a greater heat loss rate from the chemical reactions within the tube and establishes the requirement for a higher wall temperature to produce ignition. A semi-empirical equation of the form:

$$\frac{1}{T_w} = \frac{1}{T_{w,o}} - aU_s^m$$

can be obtained for the effect of flow on ignition temperature. The equation obviously has a limited range of utility since, at very large values of U_s, a negative wall temperature would be predicted.

Some data on the effect of flow on ignition temperature are presented in Figure 46 from data of Ref 28. These data are re-plotted in Figure 47.

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Figure 46. Autogenous Ignition Temperature versus Mixture Velocity at Sea Level
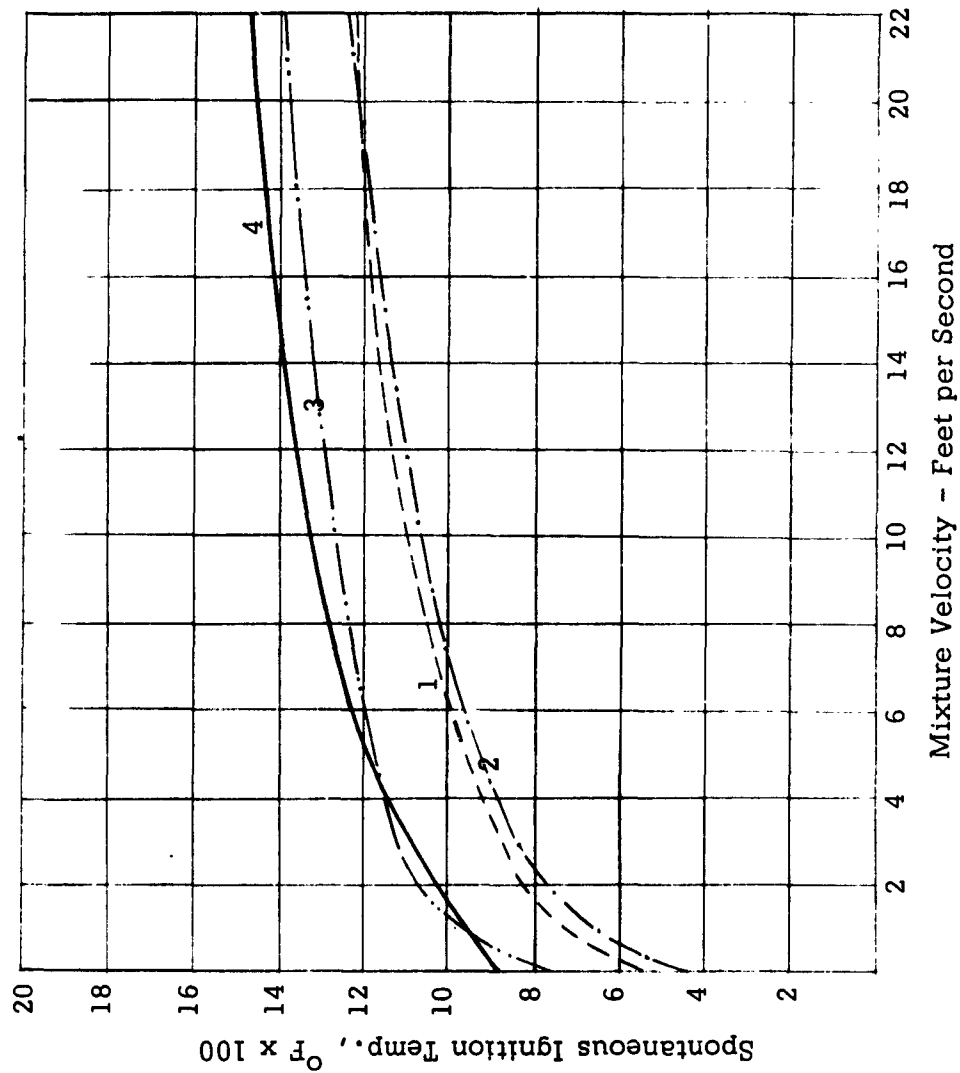
1 – JP-4 Vapor-Air
2 – Hydraulic Fluid
    MIL-0-5606
    Vapor-Air
3 – Av Gas 100/130
    Vapor-Air
4 – Av Gas 115/145
    Vapor-Air

All tests performed
with mixture flowing
through a two-inch
stainless steel pipe
three feet long

Mixture Velocity – Feet per Second

Spontaneous Ignition Temp., °F x 100

103
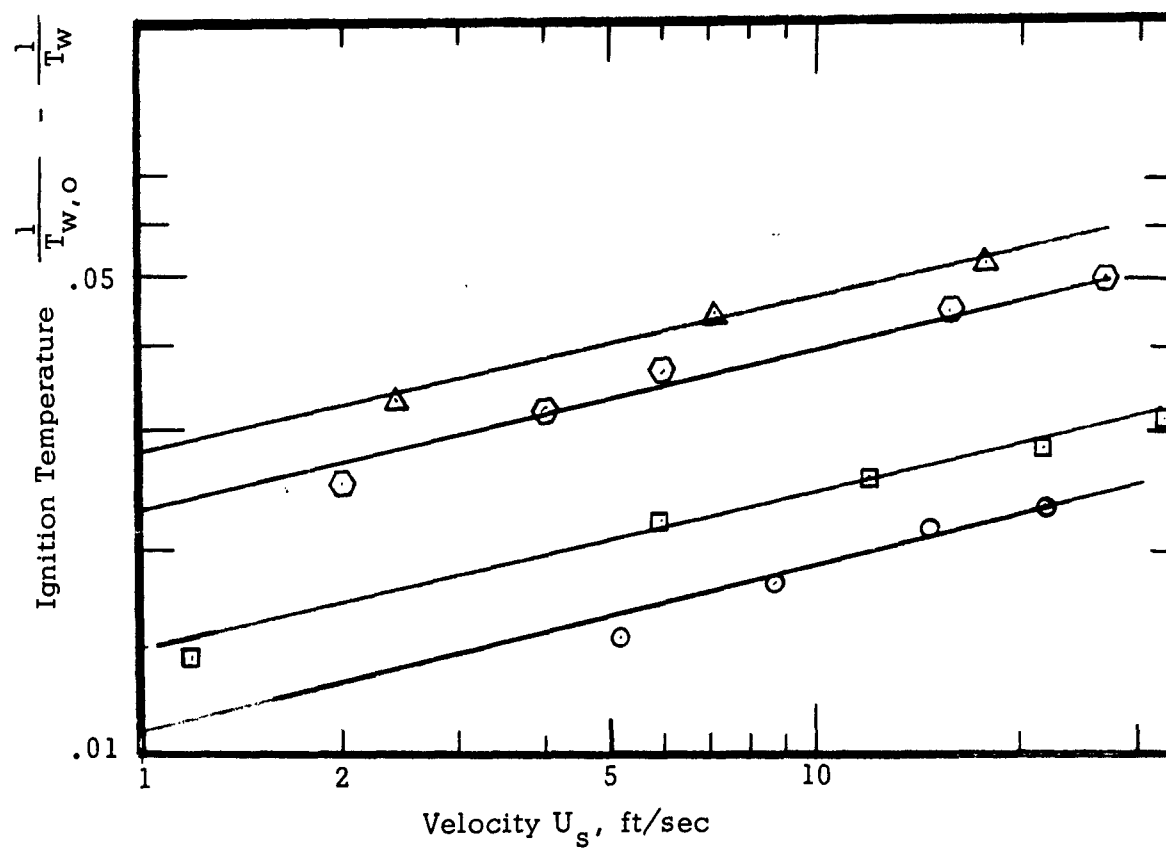
Figure 47. Correlation of Ignition Temperature Variation
with Velocity

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in terms of $\dfrac{1}{T_{w,o}} - \dfrac{1}{T_w}$ versus U_s to illustrate the fit of the correlation. From the data it appears that a value of $M = 1/4$ gives a reasonable fit so that

$$\frac{1}{T_{w,o}} - \frac{1}{T_w} = aU_s^{1/4} \tag{47}$$

where a is an empirical constant determined by the fuel involved.

In a system of limited length, another factor which involves the ignition time lag may determine the wall temperature required for ignition. We assume here that ignition must occur within the time associated with the residence of the gas near the hot surface.

This time, Υ, can be estimated by

$$\Upsilon = \frac{L}{\bar{U}_s} \tag{48}$$

where Υ = time lag

   L = length of heated surface

   $\bar{U}_s$ = mean gas velocity

Using equation (34) to obtain a relationship for   and substituting equation (48) one gets

$$T_w = \frac{E}{R} \left(\frac{1}{1 - \dfrac{\bar{U}_s}{L}} \right) + \text{constant} \tag{49}$$

which can also be written as

$$\frac{1}{T_w} = \frac{1}{T_{w,o}} \left(1 - \frac{\bar{U}_s}{L} \right) \tag{50}$$

It should be noted that equation (50) represents merely a time lag effect and does not include the change of T_w with velocity as developed earlier.

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2. Hot Gas Ignition

Another method by which ignition can be initiated is the introduction of a hot gas into a flammable mixture. This process can be of importance in fire hazard evaluation since it is possible that hot gases passing through small openings between two bays could cause ignition in an adjacent bay from a fire initiated in the first bay under conditions where the channel is sufficiently small to quench an active flame.

Hot gas ignition temperatures (Ref 37) have been measured for a series of fuels. In general the gas temperatures required for ignition are considerably above the spontaneous ignition temperatures measured in ASTM or similar equipment. The measured temperatures are a function of experimental conditions, however, so that the possibility of ignition with gases at lower temperatures than those reported in Ref 37 cannot be ruled out.

Some data for the ignition temperatures required for hot air jets into vapor fuel are given in Table 21 (Ref 37).

Table 21. Ignition Temperature for Hot Air Jets, ^{O}F

Fuel	Jet Diam, 10 mm 100 cc/sec, air	Jet Diam, 4 mm 35 cc/sec, air
Methane	1904	2174
Ethane	1544	1733
Propane	1625	1850
n-butane	1670	1877

Similar data for a hot nitrogen jet into a fuel-air mixture are given in Table 22 (Ref 37).

Table 22. Ignition Temperature for Hot N_2 Jets, ^{O}F

Fuel in Fuel-Air Mix	N_2 Jet, 10 mm 100 cc/sec	N_2 Jet, 7 mm 60 cc/sec
Methane	2417	2192
Ethane	1679	1859
Propane	1814	2030
n-butane	1814	2003

As one might surmise due to the dilution effect of the nitrogen, the ignition temperatures are somewhat higher than those obtained with an air jet. It also seems logical to expect that the required jet temperature would decrease as the fuel or fuel-air mixture temperature increases, approaching as a limit the spontaneous ignition temperature of vapor in a flowing gas type experiment.

Evidence that the ignition of a fuel by hot gas may involve a somewhat different mechanism than the usual spontaneous ignition experiments includes the lack of an effect due to iron carbonyl and tetraethyl lead. These compounds are reported (Ref 37) to have no effect on hot gas ignition although both compounds have been shown to reduce spontaneous ignition temperature.

3. Ignition of Single Drops

Some insight into the mechanism of the thermal ignition of liquid fuels may be obtained from experiments with single drops. Some work has been done, in which individual drops were rapidly inserted into the air space within a high temperature furnace (Ref 38). Surface effects are, of course, eliminated in such an experiment.

Measurements were made of the time necessary to reach steady-state evaporation, Υ_1, and the additional time for ignition to occur, Υ_2 so that the total ignition delay is given by

$$\Upsilon_{ig} = \Upsilon_1 + \Upsilon_2 \tag{51}$$

Some typical time lags for α-methyl naphthalene in air heated to various temperatures are shown in Figure 48 for various initial drop diameters. For the range of drop sizes investigated, there is apparently a change from non-ignition to ignition in the temperature range between 752°F and 1022°F. The ASTM ignition temperature for α-methyl naphthalene is 984°F. It is evident from the figure that the time necessary to reach steady-state evaporation increases with drop diameter while the time necessary for ignition, once steady-state evaporation has occurred, decreases. The overall ignition lag increases with increasing drop diameter. The increase in Υ_1 with drop diameter is easily explained. Larger drops absorb more heat before reaching a steady state. The decrease in Υ_2 as drop diameter increases is more difficult to explain. Perhaps the longer pre-heat period (Υ_1) for large drops permits the vapor to reach a higher temperature and allows more time for some of the chemical reactions leading to ignition, thus reducing the additional time required for ignition.

The region of temperature between non-ignition and ignition appears to result from two competing rates---evaporation and reaction. If the drop vaporizes completely before reaction occurs, ignition does not occur. Since

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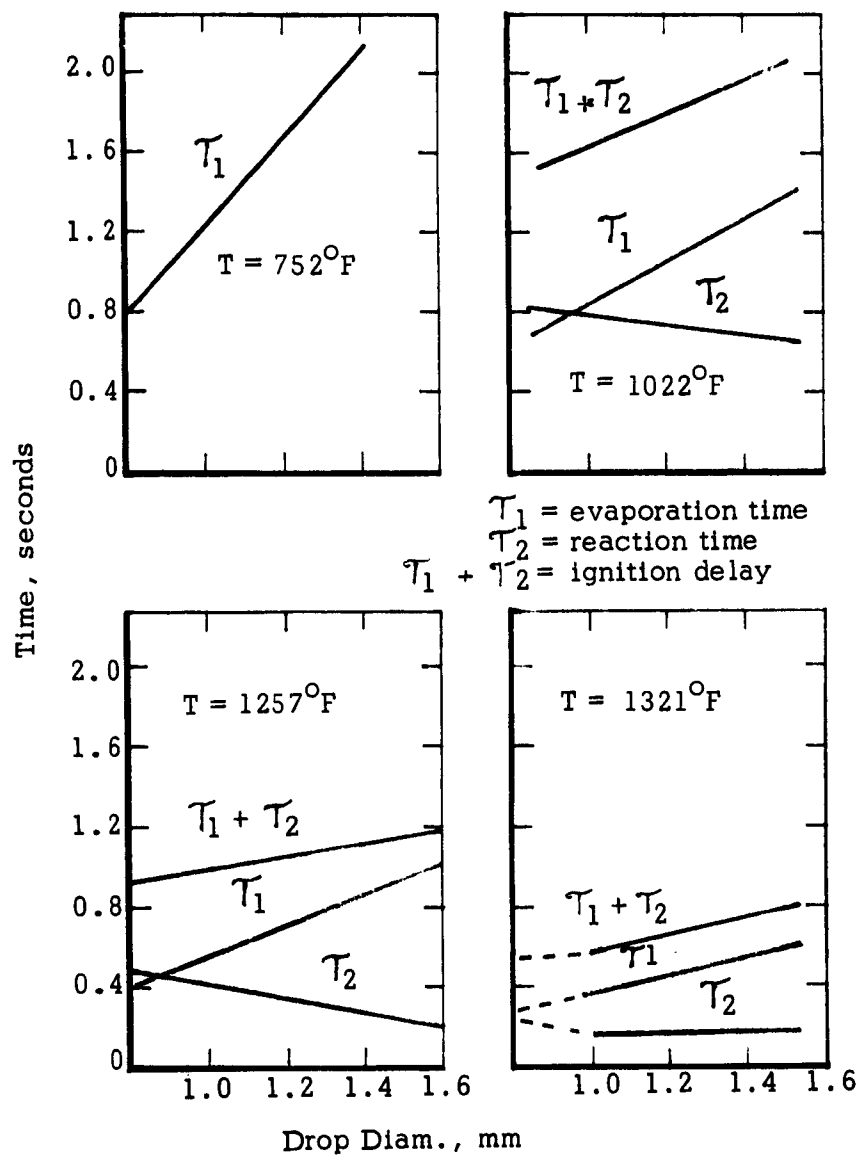
Figure 48. Single Drop Ignition Delays for α-Methylnephthalene

evaporation rate is roughly a linear function of temperature while reaction rate is an exponential function of temperature, the reaction rate increases more rapidly with temperature than the evaporation rate and an ignition temperature results. One would expect that the ignition temperature would be a function of drop size or quantity of liquid which is consistent with previous liquid injection ignition experiments.

Experiments of a similar sort (Ref 39) show that the flame is actually initiated at a point of one of the concentric layers of vapor-air mixture surrounding the drop and propagates along this layer until the drop is surrounded by a flame.

Although the ignition of single drops does not simulate a likely hazard situation it appears that the phenomenon is closely related to the spontaneous ignition process and provides useful data relative to the ignition mechanism. The results indicate the importance of vaporization in the thermal ignition of liquids, a factor which has been emphasized in the discussion of the ASTM method and which has been treated as a possible explanation of the differences in ignition temperature for chemically similar flammables of different volatility.

4. Ignition by Friction Sparks

Ignition by friction sparks represents a fire hazard that is principally associated with crash fire situations. The subject of crash fires which has been studied and reported in Ref 40 is outside the scope of the present study. Nevertheless, since friction sparks can be produced under damage conditions during flight, the major conclusions will be reviewed here.

The formation of friction sparks, produced by the contact of two surfaces has not been clearly defined or explained in spite of the common occurrence of the phenomenon. Studies of friction spark occurrence indicate that the tendency to produce sparks resulting from metal to metal contact is related to the hardness of the metal (Ref 41). Thus a ferrous alloy is more likely to spark than an aluminum alloy. Other properties of the material also appear to be related to the tendency to produce friction sparks. Such factors as the chemical reactivity of the material and shape and nature of the surface affect the tendency to form friction sparks (Ref 42).

The chemical reactivity of the material may be related to the tendency of the material to react with oxygen. It has been observed that grinding steel against corundum does not produce friction sparks in an oxygen-free atmosphere (Ref 43). The incandescence of the sparks is thus attributed to the oxidation of particles formed during contact. It is suggested that the ordinary white sparks produced when grinding a metal in air is the result of oxidation of the metallic particle which has been heated during the

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contact (Ref 44). Measurements of the temperature of friction sparks confirm such a mechanism. Typical values of the temperature of friction sparks based on spectroscopic studies show magnesium particles with a temperature of about 7000°F and titanium particles with a burning temperature of about 4500°F (Ref 45).

The nature of the surface can also affect the tendency to produce sparks as well as the tendency of the metal itself to ignite under friction conditions. Treatment of titanium with concentrated nitric acid can change the metal surface producing conditions where the metal itself will ignite as a result of either impact or friction (Ref 46). Oxide films on a surface, such as rust on ferrous materials, can also produce reaction on impact due to the reaction of one metal with the oxide of another, the so-called Thermit reaction (Refs 47, 48, 49). It has been noted, for example, that an aluminum spark adhering to fresh rust in or near the zone of impact or friction could react to produce a temperature adequate for ignition of hydrocarbon type flammables (Ref 41).

A summary of the factors which influence friction spark generation and ignition is given below:

a. Chemical compositions of contact surfaces
b. Nature of the chemical bond in each material
c. Positions of the metals in the electromotive series
d. Hardnesses of contact surfaces
e. Brittleness of the metal
f. Thermal conductivities of the materials
g. Presence of protective coatings
h. Shapes and roughnesses of the contact surfaces
i. Angle of impact
j. Energy of impact
k. Force between sliding surfaces
l. Duration of frictional contact
m. Differential velocity between surfaces
n. Temperature, size, number and electrical charge of sparks
o. Composition of the inflammable material
p. Ratio of inflammable material to oxygen

The current state-of-the-art has been summarized in Ref 50 and is presented here as a part of the supersonic transport fire hazard study. Examination of the following metals: 2024-T3 aluminum alloy, Ti-100A titanium alloy, FSI magnesium alloy, chrome molybdenum (SAE 4120) steel and AISI 347 stainless steel indicated that aluminum shows the least tendency to form friction sparks. Titanium on the other hand ignited the flammable mixture most readily. The other metals involved showed a behavior intermediate between aluminum and titanium. Little is known about the change in friction spark tendency for different titanium alloys.

There are no indications as yet that alloys of titanium have a reduced tendency toward producing friction sparks. One would expect that alloys which are less brittle than pure titanium and have improved thermal conductivity would show less friction spark tendency but this has not yet been demonstrated. In the absence of definitive experimental data it must be assumed that titanium alloys present a serious friction spark hazard compared to other metals such as aluminum and a greater friction spark hazard than stainless steel.

5. Electrical Ignition

Ignition of a fuel-air mixture by electrical sparks represents a different form of ignition from thermal ignition and the results generally do not correlate with thermal ignition temperatures. Generally, electrical ignition energies correlate better with such propagation parameters as flame velocity and quenching distance. An examination of a typical electrical ignition experiment may suggest a reason for the relationship between ignition energy and flame propagation.

In a typical experiment a spark is created between two electrodes immersed in a fuel-air mixture. The energy of the spark is varied and observations are made to determine when the spark creates a flame kernel which can propagate away from the region of the electrodes into the surrounding mixture. It is here, in the method of observation that the tie to flame propagation is first established. A spark which has sufficient energy to generate a small flame kernel which fails to propagate is not considered as having produced ignition. A higher energy spark which can produce a flame kernel capable of propagating independently into the mixture is required. The minimum spark ignition experiment thus uses a propagating flame as its criterion. This does not mean that a spark below minimum energy does not produce any chemical reaction. In some cases, in fact, a visible flame kernel which later disappears can be initiated below the accepted ignition energy.

Unlike the thermal ignition temperatures, the minimum spark ignition energy is a fairly reproducible measurement. Most of the deviations appearing in the older literature on spark ignition can be explained on the basis of failure to account for the quenching action of the electrodes and/or a discrepancy between stored energy and the actual energy delivered to the mixture. Some uncertainties still exist which are often associated with the electrical circuitry. These uncertainties may also be explained when a better understanding exists with regard to the effects of spark duration on ignition energy and the effects of discharge characteristics and electrode materials are better understood. In terms of the problem of fire hazards, however, these effects are of relatively minor importance for sparks near the minimum ignition energy. These same factors, however, may assume greater importance with respect to ignition by very high energy discharges,

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an area of electrical ignition research which has received relatively little attention.

For a given mixture, the energy required for ignition is a function of electrode variables, the most important of which is probably electrode spacing. The variation of ignition energy with electrode spacing is illustrated in Figure 49 for needle-like electrodes and for flanged electrodes. Higher energies are required for short electrode gaps, the effect of electrode spacing becoming negligible for sufficiently large gaps. The flanged electrodes show the most abrupt change. Presumably the increased energy required for small values of electrode spacing is to overcome the quenching effects of the electrodes. In the case of flanged electrodes, the flame kernel generated by the spark is apparently incapable of propagating through the finite quenching channel created by the flanges. The gap spacing at which the break in the curve occurs for flanged electrodes agrees well with quenching distances measured by other techniques. These will be discussed under the heading of quenching phenomena.

Some effects have been noted with respect to electrode material and nature of the discharge (Ref 51). These effects are generally small and are not well understood. Electrode material appears to alter ignition energy somewhat for long duration sparks and the effect might be associated with changes in the arc due to differences in electrode vaporization.

For a given combustible, the critical ignition energy is a function of the mixture composition. Typical behavior is illustrated in Figure 50 for several fuels. The data are from Ref 52. It is seen that a minimum critical ignition energy exists, the energy requirements increasing for mixtures leaner or richer than the minimum. The shift of the minimum to richer mixtures as the molecular weight of the fuel increases has not been adequately explained and represents a departure from the normal behavior of flame propagation properties. The occurrence of the minimum energy at rich mixture ratios resembles the behavior of thermal ignition but there is insufficient knowledge of both measurements to know whether a relationship actually exists.

Most hydrocarbons have minimum critical ignition energies of approximately 0.2 millijoules although, as shown in Figure 50, this minimum occurs for different mixture compositions. Some typical data are presented in Table 23.

Table 23. Critical Ignition Energies

Fuel	Min. Ign. Energy, millijoules	
	Stoich.	Minimum
Benzene	55	.22
n-butane	76	.26
Cyclohexane	138	.22
Ethane	42	.24
n-heptane	115	.24
n-hexane	95	.23
Hydrogen	2	.01
Methane	33	.29
n-pentane	82	.22
2,2,4 Trimethyl pentane (iso-octane)	29	.28
Propane	30	.26

One of the most important parameters in terms of its effect on ignition energy is pressure. The marked influence of pressure, decreases in pressure producing increases in ignition energy, is an important factor in minimizing the spark ignition hazard at high altitudes. For practical estimates the variation of ignition energy with pressure can be represented by a relationship of the form:

$$M.I.E. \sim p^{-n} \qquad (52)$$

where n is the order of 1.5 to 2 for most hydrocarbons. The variation of ignition energy with pressure for a series of hydrocarbons is illustrated in Figure 51 (Ref 52). The pronounced increase in the required energy for ignition as the pressure is decreased can be of major importance in electrical ignition hazards during high altitude flight.

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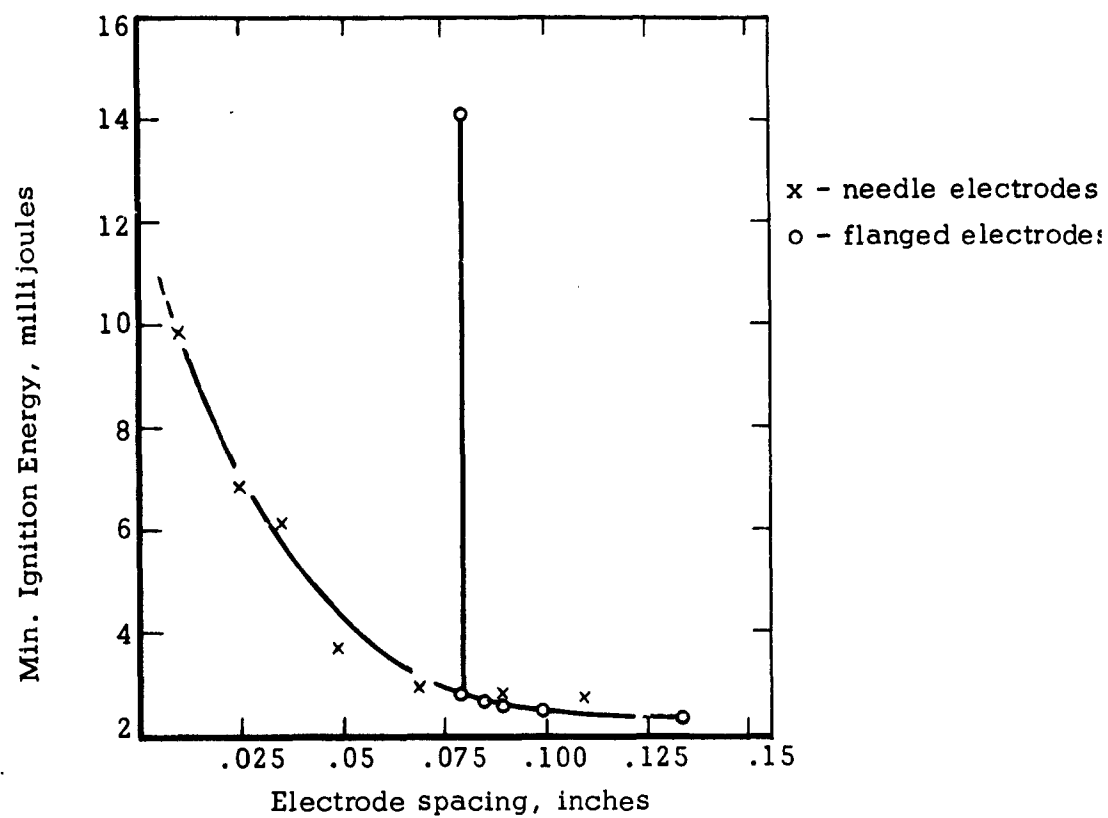
Figure 49. Variation of Ignition Energy with Electrode Spacing
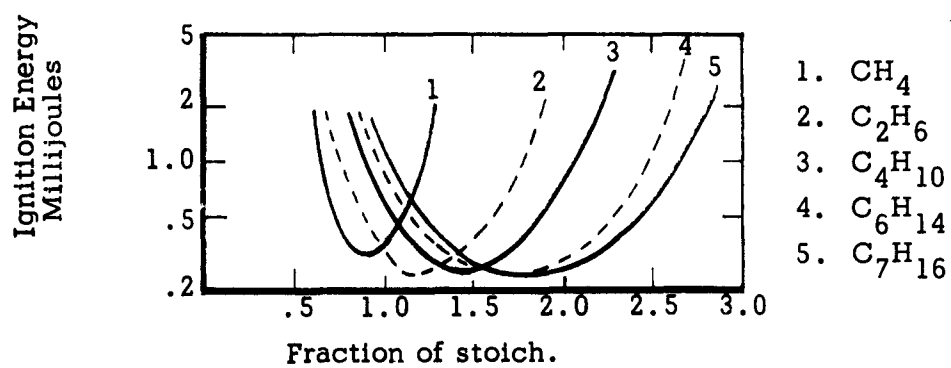
Figure 50. Critical Ignition Energy

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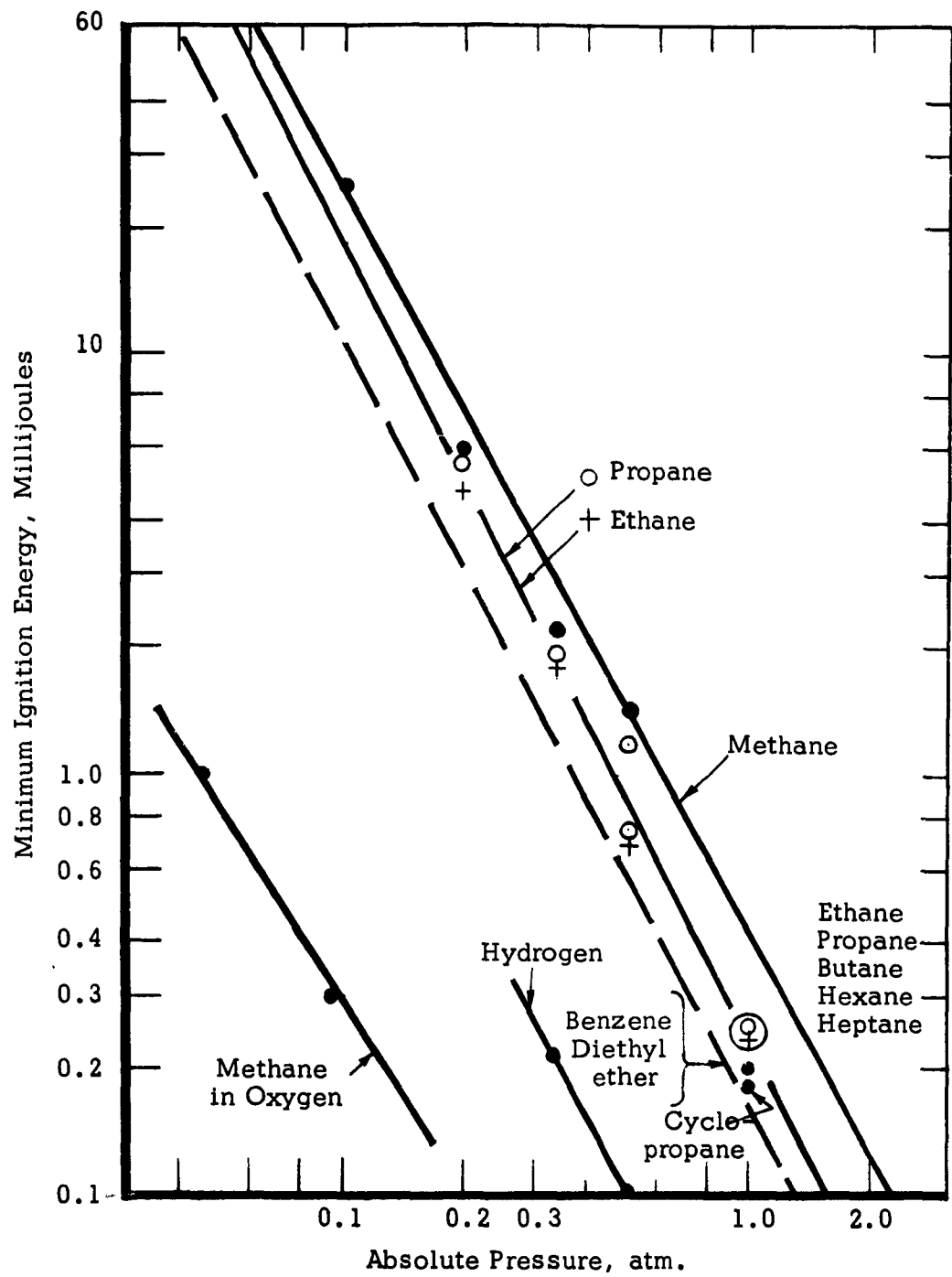
Figure 51. Relation of Minimum Ignition Energy to Static
Pressure for Hydrocarbon Fuels in Air

The effect of temperature on ignition energy has also been measured. As might be expected, increasing the temperature of the mixture leads to a lower required energy. Some typical data are presented in Table 24 (Ref 51). These data are presented in terms of the room temperature value as 1 since the absolute values differed from those generally accepted although the trends were valid.

Table 24. Variation of Critical Ignition Energy with Temperature

Fuel	Temperature $^\circ$F	Ignition Energy, Relative*
n-heptane	77	1.00
	212	.46
	340	.22
iso-octane	77	1.00
	212	.41
	340	.18
n-pentane	-22	5.77
	- 4	1.86
	777	1.00
	212	.54
	340	.30
	347	.32
propane	-40	2.15
	-22	1.76
	- 4	1.53
	77	1.00
	135	.76
	180	.65
	212	.63
	399	.25

* Ratio of Ignition Energy to Ignition Energy at 77°F for minimum energy.

Correlations of the type

$$E_{ig} = c_1 e^{c_2 T} \tag{53}$$

where c_1 and c_2 are empirical constants, have been used to represent the temperature dependence. A reasonable fit of the data in Table 24 is the equation:

$$E_{rel} = 1.59 \times 10^8 T^{-3} \tag{54}$$

Mixture velocity also has an effect on critical ignition energy, increased flow velocity leading to increased energy requirements. The effects of mixture velocity have been represented by an equation of the form (Ref 53):

$$E_{ig} = c \, \frac{U_g t_s}{p} \, \log \frac{s}{2 U_g t_s + s} \tag{55}$$

where U_g = gas velocity

t_s = spark duration

p = pressure

s = gap spacing

c = empirical constant

In the velocity range from 100 to 250 feet per second, a linear variation between E_{ig} and U_g is reasonably precise.

6.   Quenching Distance

The ability of a flame to propagate as a self-sustaining reaction requires that heat be transmitted from the flame to the unburned gas ahead of it. Abstraction of heat from the flame by the surroundings can affect the ability of the flame to propagate. Such an effect was evident in Figure 49 where the use of flanged electrodes at a critical spacing made ignition difficult to achieve. The most direct approach to the quenching phenomenon is to assume that a flame must liberate some critical quantity of heat or, an equivalent statement, that a critical flame propagation is not possible.

If the concept of a critical flame temperature is adopted then one may equate the heat loss rate to the heat generation rate as a means of establishing a thermal concept of quenching. A simplified form of the quenching equation which results from such a heat balance is (Ref 54):

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$$d^2 = \frac{G \lambda_q X_o}{C_p \overline{w}} \left(\frac{T_q - T_o}{T_f - T_o} \right) \qquad (56)$$

where d = quenching distance

G = geometric factor

λ_q = thermal conductivity

X_o = mal fraction of fuel

C_p = specific heat

$\overline{w}$ = mean reaction rate

T_q = critical temperature for quenching

T_o = initial temperature

T_f = flame temperature

The quantity G represents a conversion factor which takes into account the geometry in which the heat transfer process is taking place. The relationship for the factor G for several elementary shapes is:

$$\frac{d_p^2}{12} = \frac{d_c^2}{32} = \frac{d_r^2}{12} \left[1 - 0.3 \left(\frac{d_r}{b_r} \right) - 0.047 \left(\frac{d_r}{b_r} \right)^2 \right]^2 \qquad (57)$$

$$= \frac{d_a^2}{32} \left[1 + \left(\frac{a}{d_a} \right)^2 + \frac{1 - \left(a/d_a \right)^2}{\log_e \left(a/d_a \right)} \right] \qquad (58)$$

$$= \frac{d_e^2}{32} \left[\frac{2}{1 + \left(d_e/b_e \right)^2} \right] \qquad (59)$$

$$= \frac{d_t^2}{80} \qquad (60)$$

where
d_p = distance between plane parallel plates

d_c = diameter of a cylinder

d_r = width of a rectangular slot

b_r = length of a rectangular slot

d_a = outside diameter of a cylindrical annulus

a = inside diameter of a cylindrical annulus

d_e = minor axis of ellipse

b_e = major axis of ellipse

d_t = side length of equilateral triangle

Quenching distance varies with fuel type and fuel-air ratio. Typical variations are illustrated in Figure 52, Ref 55. It is evident that a minimum quenching distance exists at a specific fuel-air ratio. Some typical values of this minimum quenching distance for hydrocarbons are given in Table 25 from data in Ref 51.

Table 25. Parallel Plate Quenching Distance for Pure Hydrocarbons

Hydrocarbon	d_p, inches	
	Stoichiometric	Minimum
Benzene	.11	.07
1,3-Butadiene	.07	.05
n-Butane	.12	.07
Ethane	.09	.07
n-Heptane	.15	.07
n-Hexane	.14	.07
Methane	.10	.08
n-Pentane	.13	.07
Propane	.08	.07

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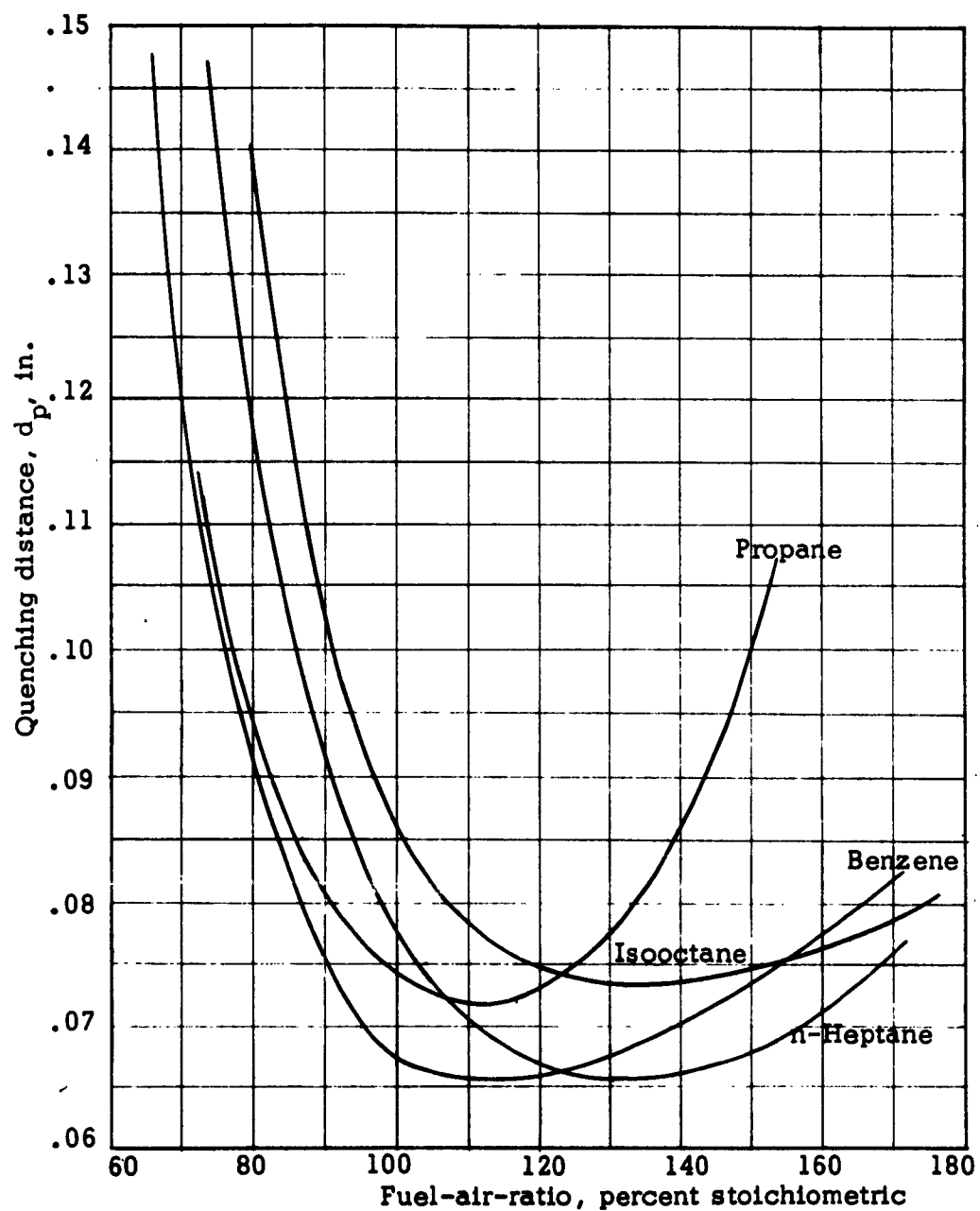
Figure 52. Variation of Quenching Distance with Hydrocarbon Type; Pressure, atmospheric; temperature, 212°F

While some variation exists in the stoichiometric quenching distance for hydrocarbons, the minimum value of .07 inches is fairly typical.

The dependence of quenching distance on reaction rate implies a dependence of quenching distance on pressure. From the relationship

$$d_p \sim \frac{1}{\sqrt{\bar{w}}} \qquad (61)$$

we can estimate that

$$d_p \sim \frac{1}{P} \qquad (62)$$

for a second order reaction. Such a dependence is found to be fairly reliable for hydrocarbons and the variation of quenching distance with the reciprocal of the pressure is a fairly useful rule of thumb.

The effect of increased temperature is a reduction in quenching distance due principally to the exponential increase in reaction rate with temperature. The variation with temperature is illustrated in Figure 53 (Ref 56). In some cases it is possible for the fuel-air mixture to exist at a lower temperature than the quenching surface. A common situation in which this occurs is the case of a flame seated on a tube. As the tube heats up the flame can enter the tube which normally would quench it due to a decrease in quenching distance with tube wall temperature. Such an effect is illustrated in Figure 54 (Ref 56).

The change of quenching distance with wall and gas temperature is an important consideration in the use of flame arrestors since an arrestor designed on the basis of a given temperature may not be effective if either the gas or the tube walls or both increase in temperature during operation.

Quenching distances are generally measured under quiescent gas conditions so that no consideration is given to the effect of gas flow on the quenching phenomenon. Although no specific data were available at the time of this report, it is fairly evident that the conduction of heat from a flame requires time. If the flow velocity is sufficiently high so that adequate residence time does not exist in a given channel, it is reasonable to expect that a flame can be blown through a channel that would quench the flame under quiescent conditions.

7.   Flammability Limits

Examination of the data for minimum ignition energy and quenching distance as functions of fuel-air composition shows that ignition rapidly requires extremely high energies and quenching occurs in tubes of extremely
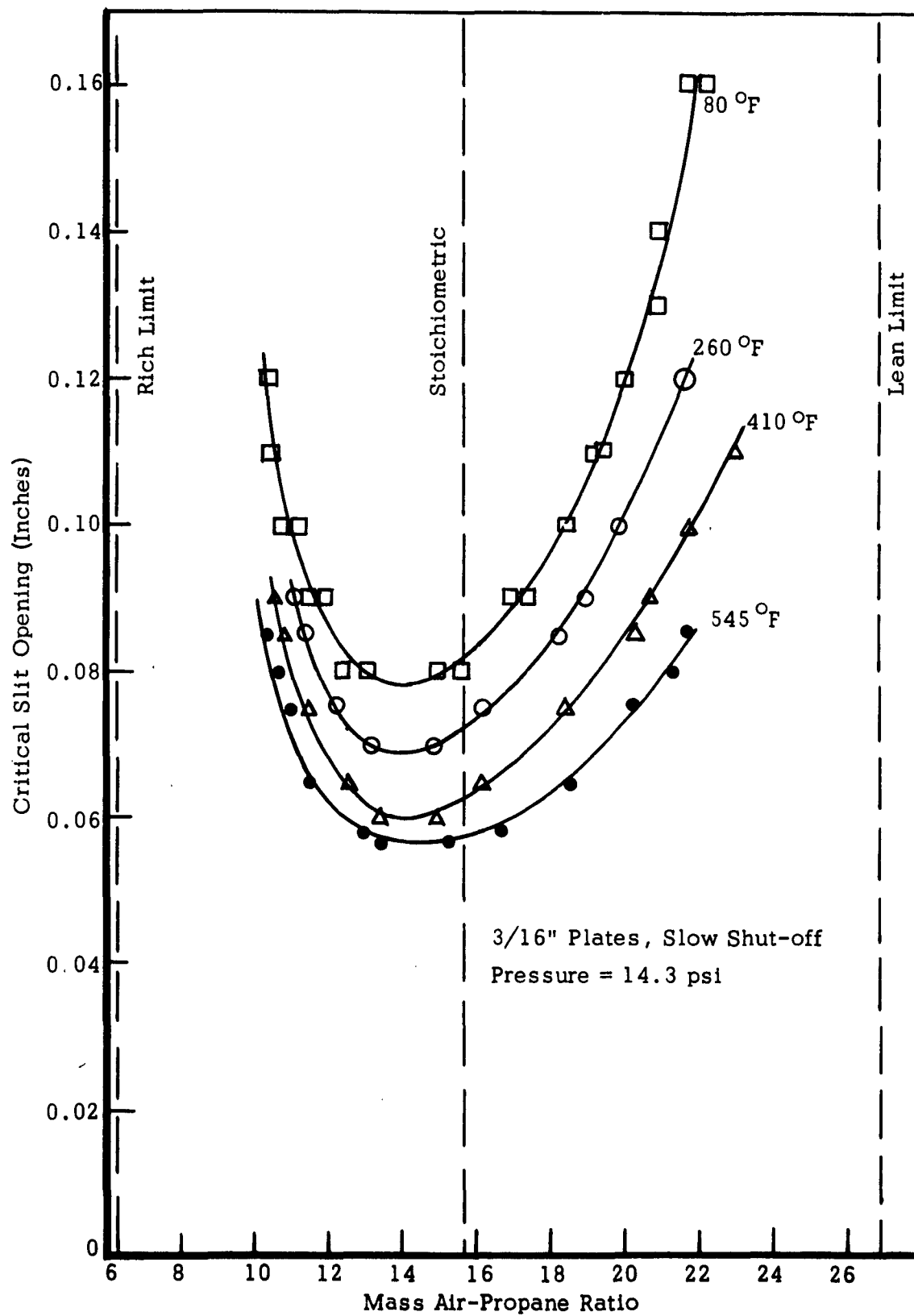
Figure 53. Quenching Effect of Propane-Air Flames with Various Inlet Temperatures (Gas and Plates at Same Temperature)
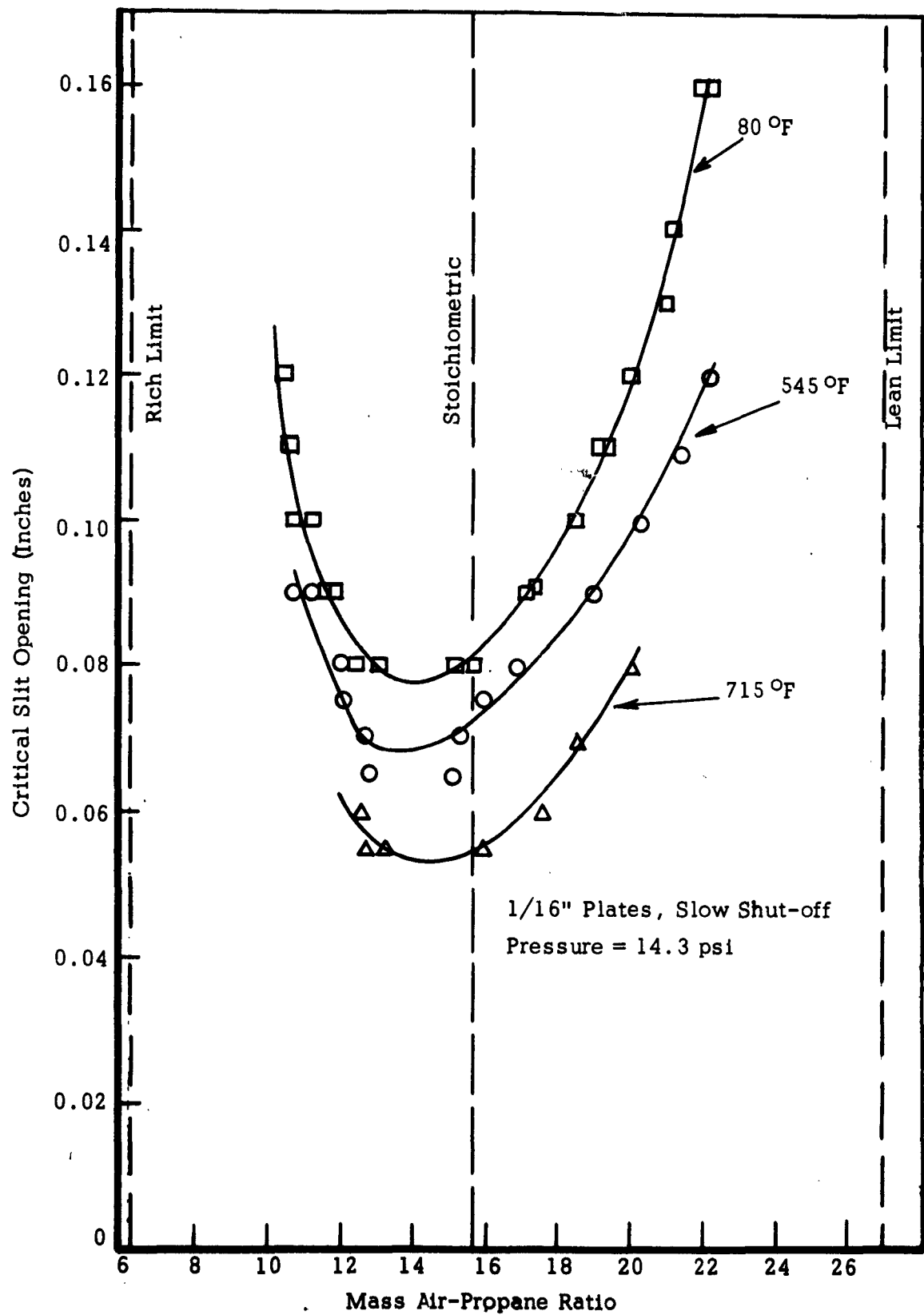
Figure 54. Quenching Effect of Propane-Air Flames with Various Plate Temperatures (Gas Initially 80°F)

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large size as certain lean and rich compositions are approached. Apparently it is not possible to ignite or propagate a flame outside of certain limits of composition. These limits are normally measured by determining the mixture composition, lean and rich which do not permit a self-sustaining flame. They are called lean and rich flammability limits.

The experimental procedure is important in determining flammability limits. The ignition source must be adequate to produce a flame if one can exist but not so energetic that the properties (particularly temperature and energy content) of the mixture are altered. The tube size must be sufficiently large that quenching plays a role in the energy balance.

Some typical flammability limits for hydrocarbons are given in Table 26 (Ref 57).

Table 26. Flammability Limits in Air at Atmospheric
Pressure and Room Temperature

Fuel	Lean Limit		Rich Limit	
	Volume percent	Fuel-air ratio, percent stoich.	Volume percent	Fuel-air ratio, percent stoich.
n-Paraffins				
Methane	5.3	53.5	14	156
Propane	2.2	53.8	9.5	251
Butane	1.9	60.1	8.5	288
Pentane	1.5	58.2	7.8	323
Hexane	1.2	55.2	7.5	368
Heptane	1.2	63.9	6.7	378
Octane	1.0	60.3	----	---
Isoparafins				
2,2-Dimethylpropane	1.4	54.2	7.5	201
2-Methylpentane	1.2	55.2	7.0	342
2,2,4-Trimethylpentane	1.1	66.3	----	---
2,2,3,3-Tetramethylpentane	.8	53.9	4.9	345
Olefins				
Ethene	3.1	45.8	32	676
Propene	2.4	52.8	10.3	247
1-Butene	1.6	46.8	9.3	294
Aromatics				
Benzene	1.4	50.9	7.1	275
Toluene	1.4	61.1	----	---
Ethylbenzene	1.0	50.7	----	---

Typical values for commercial aircraft fuels are shown in Table 27 (Ref 58).

Table 27. Flammability Limits of Typical Petroleum Fuels

| Fuel | Flammability Limits | | | |
| | Volume % | | F/A | |
	Lean	Rich	Lean	Rich
JP-1				
Minimum Volatility	0.62	4.66	0.035	0.28
Maximum Volatility	0.71	5.15	.035	0.27
Average Volatility	0.67	4.96	.035	0.27
JP-3				
Minimum Volatility	.76	5.40	.035	.26
Maximum Volatility	1.70	7.16	.035	.25
Average Volatility	.90	6.15	.035	.25
JP-4				
Minimum Volatility	.74	5.74	.035	.28
Maximum Volatility	.90	6.15	.035	.28
Average Volatility	.80	5.63	.035	.28
JP-5				
Minimum Volatility	.57	4.38	.035	.28
Maximum Volatility	.62	4.68	.035	.28
Average Volatility	.60	4.53	.035	.28
JP-6	.6	3.7	.035	.28
#1 Fuel Oil				
Minimum Volatility	.53	4.18	.035	.28
Maximum Volatility	.61	4.61	.035	.29
Average Volatility	.58	4.45	.035	.28
#2 Fuel Oil	.52	4.09	.035	.29
#4 Fuel Oil	.45	3.71	.035	.29

In general the flammability of commercial hydrocarbon fuels and oils can be estimated by making use of the correlations relating to molecular weight and using the limit data for the pure hydrocarbon having the same molecular weight.

The lean limit for hydrocarbons may be estimated from the following expression:

$$L_V = \frac{1.87 \times 10^6}{q_N \ M} \tag{63}$$

where L_V = lean limit, volume %

q_N = net heat of combustion, Btu/lb

M = molecular weight

In terms of fuel-air ratio, the equation becomes

$$L_{f/a} = \frac{L_V \quad M}{(100 - L_V) \ (28.97)} \tag{64}$$

The rich limit can be estimated from

$$R_V = L_V + \frac{143}{M^{0.7}} \tag{65}$$

or

$$R_{f/a} = \frac{R_V \quad M}{(100 - R_V)(28.97)} \tag{66}$$

The measured flammability limit can be a function of tube size and pressure as shown for the lean limit in Figure 55 (Ref 59). At high levels of pressure, the lean limit concentration decreases as tube size increases, approaching an asymptotic value. The low pressure behavior appears to follow the same trend but larger tube sizes are required to reach the asymptotic value as the pressure decreases. Clearly, there is a quenching effect due to the tube walls until a sufficiently large tube is reached.

For each tube size there is a pressure limit below which flame propagation will not occur. These tube sizes represent the quenching distance for the mixture and pressure concerned. Comparison of quenching distances and critical pressure limits shows that a good correlation exists (Ref 60). It is important, therefore, that the interpretation of low pressure flammability limit data include possible effects of geometry and size.

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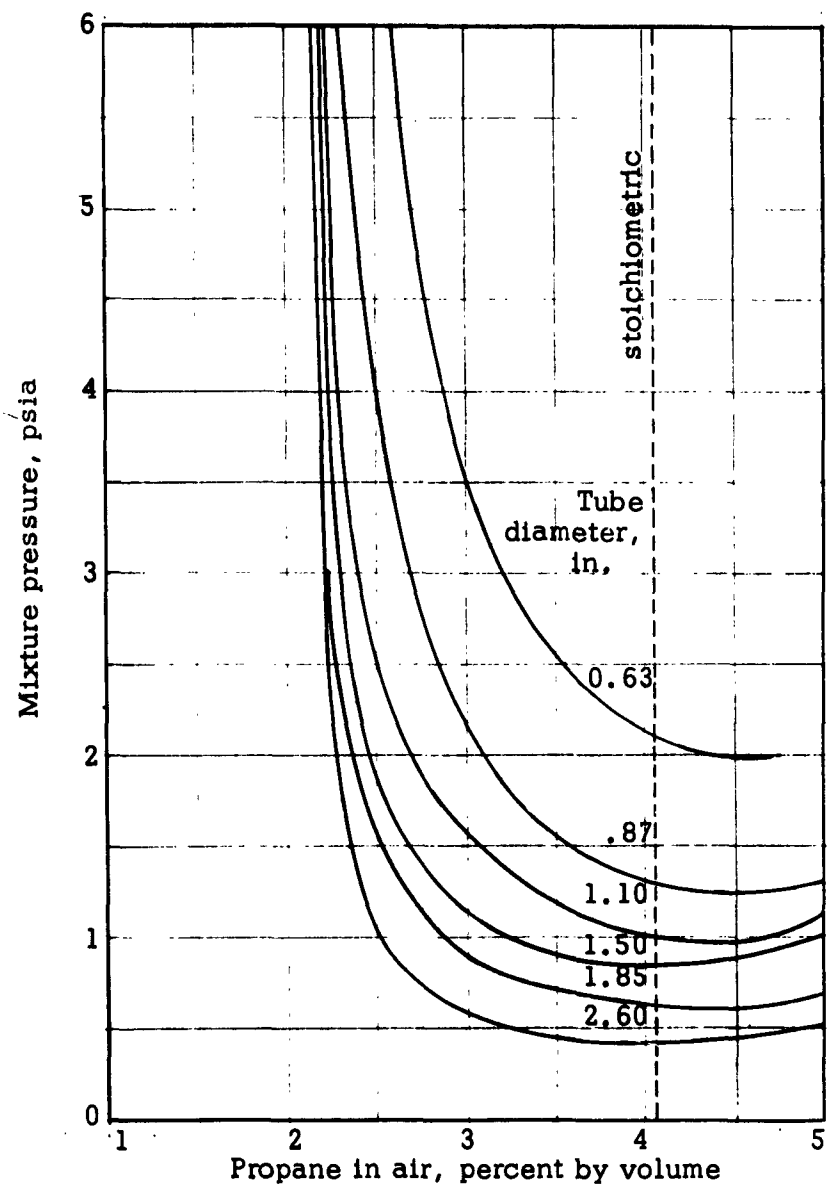
Figure 55. Effect of Tube Diameter on Low-Pressure Limits of
Flame Propagation

There does appear to be a set of flammability limits which are independent of tube size. These limits appear to be very insensitive to pressure if the experiment is conducted in a tube with a sufficiently large diameter.

Increasing the initial temperature broadens the flammability limits but the effect is not large. Increasing temperature moves the lean flammability limit to lower fuel concentrations and the rich flammability limit to higher fuel concentrations, producing a broader flammability range. For n-pentane, the following change is noted for the flammability limits, Table 28 (Ref 56).

Table 28. Effect of Temperature on Flammability
Limit of n-Pentane

Temperature °F	Limit Concentration % by Volume	
	Lean	Rich
63	1.53	4.50
570	1.22	5.35

The effect of temperature on limit concentration is approximately given by a linear relationship. The following equations can be used for estimates of the effect of temperature (Ref 61):

$$\text{Lean Limit} \quad (V_L)_{T_2} - (V_L)_{T_1} = -6.1 \times 10^{-4} (T_2 - T_1) \qquad (67)$$

$$\text{Rich Limit} \quad (V_R)_{T_2} - (V_R)_T = 17 \times 10^{-4} (T_2 - T_1) \qquad (68)$$

where V_L = lean limit concentration, volume %

V_R = rich limit concentration, volume %

A useful method of describing the flammability characteristics of a fuel is to prepare a diagram which includes the vapor pressure of the fuel and the temperature to which the fuel is exposed. Such diagrams are illustrated in Figures 56 and 57 (Ref 62). The diagram has been prepared for a pressure of 1 atmosphere. A similar diagram for lower pressures would exist with the limit concentrations unchanged for large containers and the spontaneous ignition temperature increased as the pressure decreases.

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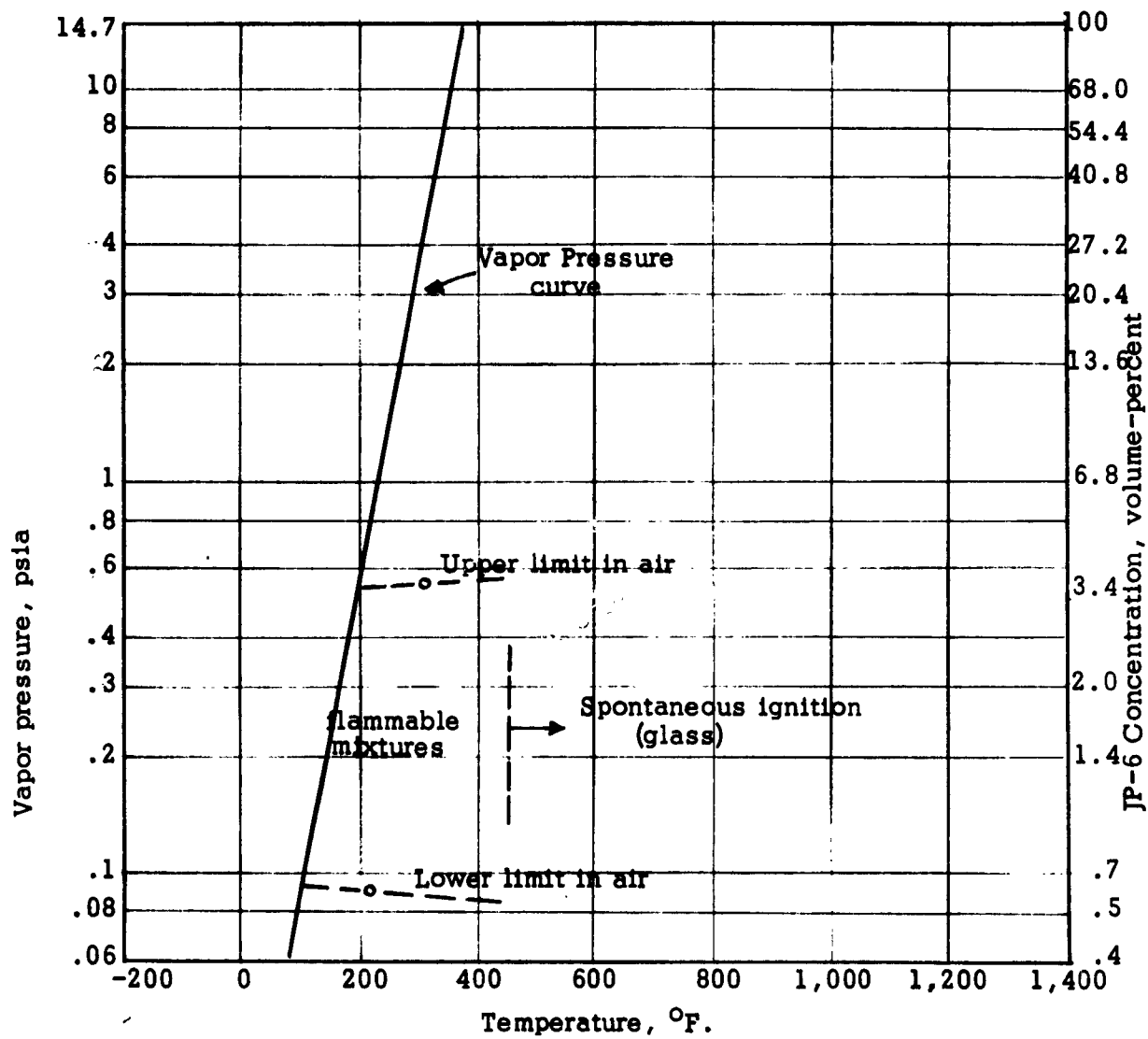
Figure 56. Flammability Characteristics Diagram of JP-6 in Air
at Atmospheric Pressure
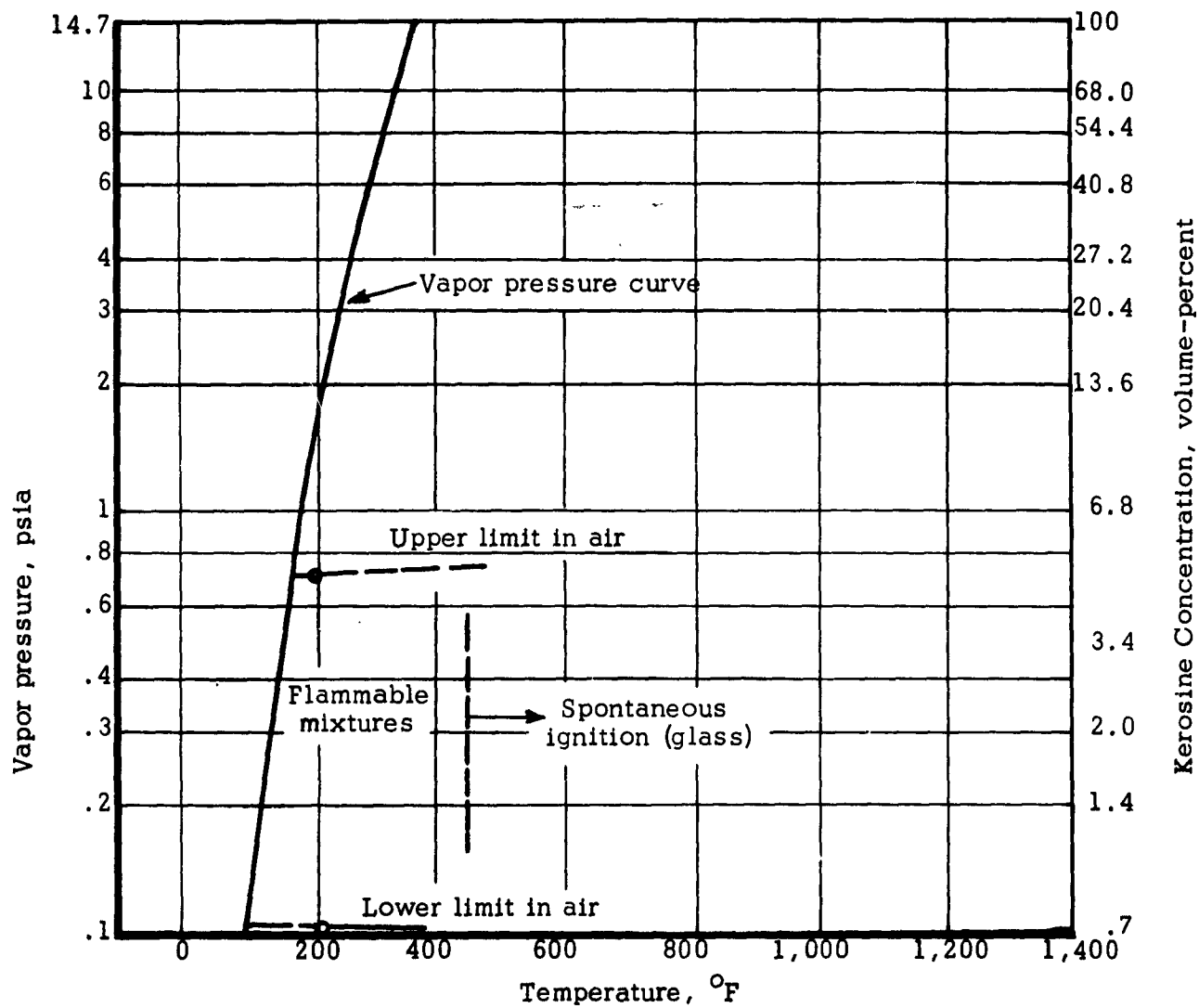
Figure 57. Flammability Characteristics Diagram of Kerosine in Air at Atmospheric Pressure

8. Flame Propagation

The rate at which flame will propagate through a combustible mixture depends on the composition of the mixture as well as on the environmental conditions. In order to establish a flame propagation rate reasonably independent of apparatus effects, a property called normal flame velocity or burning velocity has been defined. The normal flame velocity or burning velocity represents the rate at which a flame propagates into a static gas mixture perpendicular to the surface of the flame. Conversely, one can consider the velocity of the gas which passes through a flat flame fixed in space and with a surface perpendicular to the uniform gas flow. Burning velocity is deduced from laboratory measurements using Bunsen burner flames, flames propagating in tubes, in soap bubbles and in constant volume bombs. In each type of experiment, a rate of flame propagation is measured and the burning velocity calculated. The burning velocity is a function of the mixture composition including the nature and concentration of fuel, concentration of air or other oxidant and the concentration of additives, contaminants or diluents. The burning velocity is reasonably independent of such experimental factors as gas flow rate, size of flame, shape of flame, direction of propagation, etc. The burning velocity does depend on temperature and pressure. The burning velocity thus serves as a burning rate or propagation rate index or coefficient from which propagation rates can be estimated.

Burning velocity, for a given fuel in air, varies with the mixture composition as shown in Figure 58. The data have been plotted as

$$U_f/(U_f)_{max} \quad \text{versus} \quad \phi/\phi_{max}$$

since the shape of the burning velocity versus curve is similar for different fuels. The curve is suitable for both laminar and turbulent flames. The equation which fits the curve is:

$$1 - \frac{U_f}{U_{f,max}} = 4.5 \left(\frac{\phi}{\phi_{max}} - 1\right)^2 \tag{69}$$

where U_f = burning velocity

ϕ = equivalence ratio: $\frac{F/A}{(F/A) \text{ stoich}}$

If the maximum burning velocity and fuel-air ratio are known, the remainder of the curve can be reconstructed. The variation of burning velocity with fuel type can be seen from the data of Table 29 (Ref 61).

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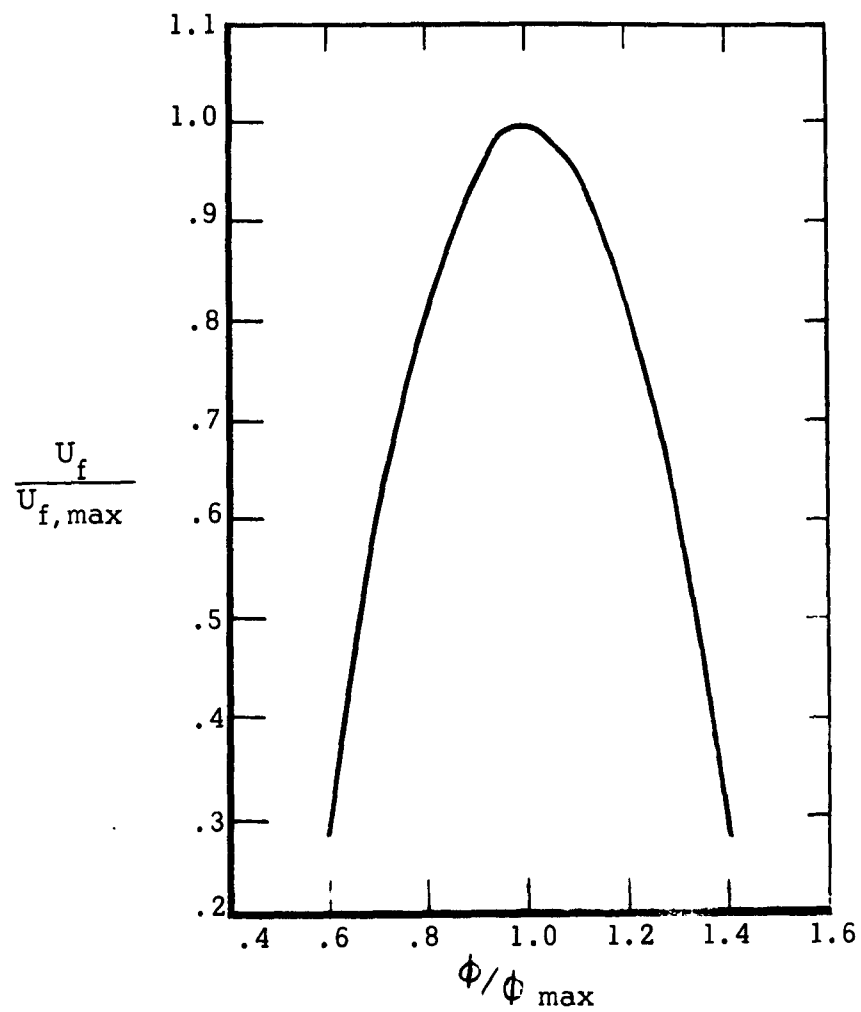
Figure 58. Variation of Ratio $U_f/U_{f,max}$ with ϕ/ϕ_{max} for Laminar and Turbulent Flames of Methane and Butane

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Table 29. Maximum Burning Velocities for Typical Fuels

Fuel	$U_{f, max,}$ ft/sec	ϕ_{max}
Propane	1.41	1.14
n-Pentane	1.40	1.15
n-Hexane	1.40	1.17
n-Heptane	1.40	1.22
iso-Octane	1.25	1.17
100-octane Gasoline	1.24	1.06
JP-1	1.21	1.07
JP-4	1.25	1.07

It is evident that there is only a small effect of hydrocarbon type on maximum burning velocity and that a value of $U_{f, max}$ = 1.2 ft/sec and ϕ_{max} = 1.1 mixed fuels if actual measured values were not available.

The effect of pressure on burning velocity has been the subject of much investigation. It has not often been possible to separate apparatus effects from the results of experimental measurements. Such apparatus effects include quenching by surfaces near the flame which reduces the measured velocity compared to the "true" burning velocity and changes in flame thickness which affects the calculation of burning velocity from the measured propagation rates. Typical variations of burning velocity with pressure for two hydrocarbons are summarized in Table 30 (Ref 61).

Table 30. Effect of Pressure on Burning Velocity

Fuel	Equivalence Ratio	Pressure Range atm.	Pressure Dependence
n-Heptane	1.0	0.53 - 0.99	p - 0.36
Iso octane	1.0	0.53 - 0.92	p - 0.39

It appears that a variation of the order of

$$U_f \sim p^{-1/3} \quad \text{(1/2 to 1 atm)} \tag{70}$$

would represent a reasonable approximation for hydrocarbon fuels, unless reliable experimental data were available. Other data suggest no pressure dependence below 1/2 atmosphere and possibly a decrease below 1/4 atmosphere. On this basis a variation in burning velocity from 1.2 ft/sec at sea level to 1.5 ft/sec at 20,000 ft and constant at 1.5 ft/sec at higher altitudes would represent a reasonable estimate for the pressure environment of the supersonic transport.

Initial mixture temperature has a very marked effect on burning velocity. The variation of burning velocity with temperature for propane-air is illustrated in Figure 59. In the range of temperature from 360° to 1100°R ($\pm 100^\circ$ to 640°F) the temperature variation of burning velocity can be represented by:

$$\frac{U_{f,t}}{U_{f,o}} = 0.25 + 2.6 \times 10^{-6} \, T^2 \tag{71}$$

where T = initial temperature, $^\circ$R

$U_{f,t}$ = burning velocity at temperature, T

$U_{f,o}$ = burning velocity at 537°R (77°F)

Since propane is a fairly representative hydrocarbon, most jet fuels would be reasonably well represented by the above equation.

Some care must be exercised in the estimation of temperature effects on burning velocity in the temperature range where oxidation occurs. If partial oxidation occurs before the mixture burns, the burning velocity is affected. An illustration of such an effect is presented in Figure 60 from Ref 63.

At a contact time of 5 seconds, the burning velocity reaches a maximum and then decreases due to pre-reaction. Presumably, the decrease in burning velocity would occur at lower initial temperatures for longer contact times or for more easily oxidized fuels.

Burning velocity is relatively insensitive to small quantities of additives including those which show a marked effect on ignition temperature. Additives such as tetraethyl lead and iron carbonyl showed no effect on the burning velocities of twenty fuels of various types (Ref 64). Burning velocity

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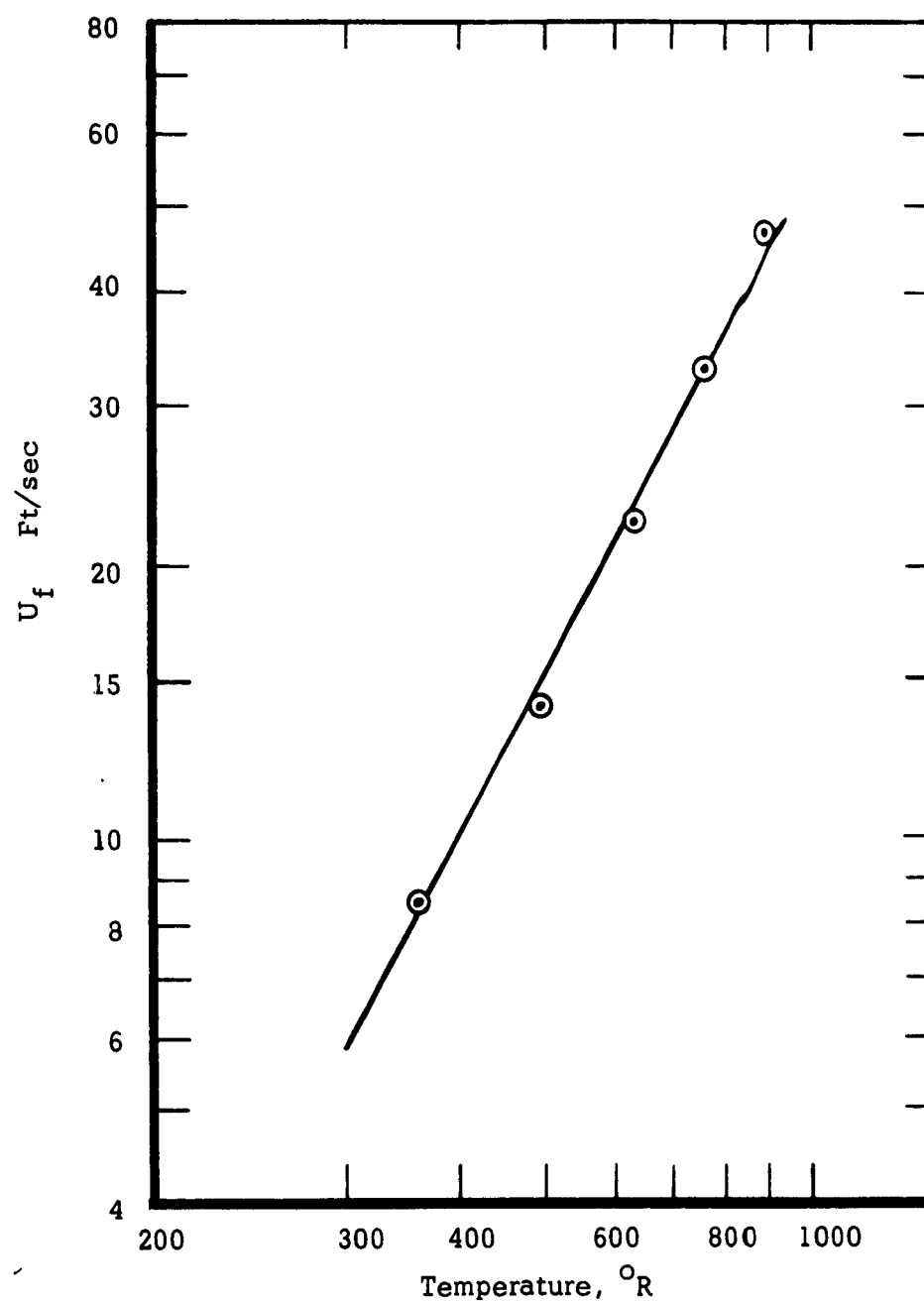
Figure 59. Effect of Temperature on Burning Velocity
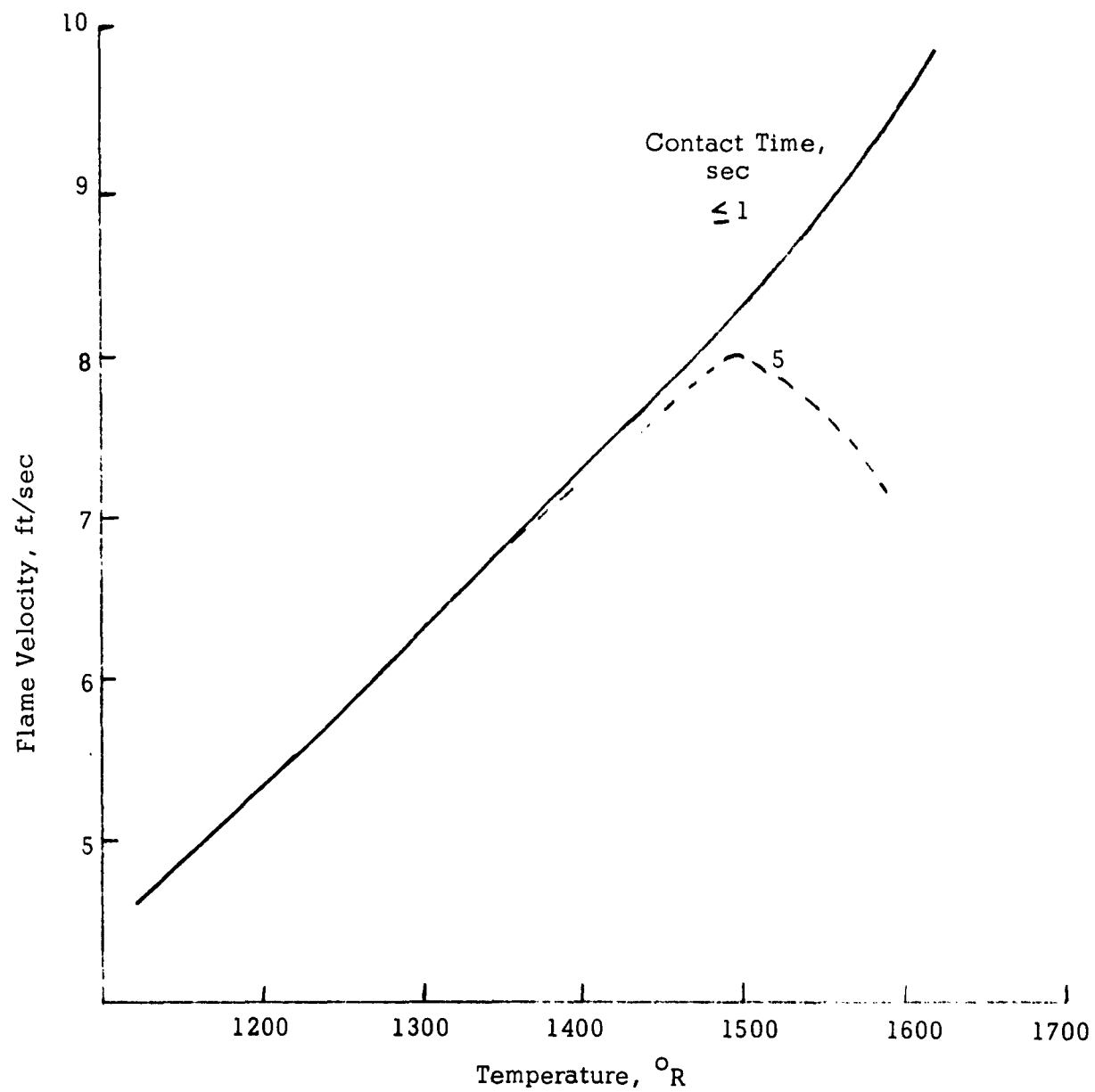
Figure 60. Flame Velocity versus Initial Mixture Temperature at an Equivalence Ratio of 1.15

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is affected, however, by changes in the oxygen-nitrogen ratio, principally due to the effect of oxygen content on flame temperature. The effect of changes in oxygen content can be described by an equation such as:

$$U_f = U_{f,air} \left[12 \ (\psi - .12) \right] \tag{72}$$

where $\quad \psi = \dfrac{O_2}{O_2 + N_2} \quad$ mol ratio

The equation shows the burning velocity falling to zero when the oxygen content is 12 mol percent.

The rate of flame propagation can be derived, in most cases, from the burning velocity. The quantity $\rho_o U_f$ represents the mass burning rate, m_o, in pounds of mixture consumed per unit area, per unit time, where ρ_o is the density of the unburned mixture. The quantity $m_o A_f$ represents the mass of combustible mixture (fuel and air) consumed per unit time in a flame have a surface area, A_f.

For the case of a flame propagating from the open end of a tube to the closed end, the rate of flame propagation is given by

$$U = U_f \times \frac{A_f}{A_t} \tag{73}$$

where $\quad U \quad$ = rate of flame propagation

$\quad U_f \quad$ = burning velocity

$\quad A_f \quad$ = area of flame

$\quad A_t \quad$ = cross sectional area of tube

The quantity A_f, however, is generally unknown unless determined experimentally. A very rough approximation of the flame surface area can be made by assuming that the flame has a hemispherical shape with a base diameter equal to the diameter of the tube. On this basis one would estimate:

$$A_f = 2\pi r^2 \tag{74}$$

$$A_t = \pi r^2 \tag{75}$$

which would result in

$$U = 2U_f \tag{76}$$

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as a very rough approximation. A somewhat more precise estimate is made if it is assumed that the flame is a parabaloid of revolution which gives (Ref 21):

$$U = 1.86 \, U_f \tag{77}$$

Such calculations give a crude estimate of the rate of propagation of a semi-confined flame in a tube or pipe open at the end from which the flame progresses.

Another condition involving unconfined or semi-confined flames occurs if a flame is initiated in a large vented space. The flame propagates, in the absence of interference by walls or air currents, as a sphere. The unburned gas is forced away from the flame and the burned gases within the flame boundary expand forcing the flame to progress at a velocity higher than normal. For such a case, the rate of flame propagation is given by

$$U = U_f \, \xi \tag{78}$$

where ξ is the expansion ratio

can be estimated from the ideal temperature rise by assuming complete combustion and perfect gas behavior, and neglecting the change in number of moles of gas.

$$\xi = \frac{T_{eq}}{T_o} = \frac{\rho_{eq}}{\rho_o} \tag{79}$$

where T_o = initial mixture temperature

T_{eq} = equilibrium flame temperature

ρ_{eq} = equilibrium density at flame temperature

ρ_o = initial mixture density

In general the effect of gas flow on flame propagation rate can be treated simply by adding the flow velocity to the flame propagation rate if they occur in the same direction or subtracting the flow velocity from the flame propagation rate if they occur in opposite directions.

The situation changes, however, if the flow is turbulent or if, in the absence of a flowing mixture, the flame area changes due to instability of the flame front or flame generated disturbances. These latter, flame in-duced effects, cannot be estimated and no theory exists which assists in predicting their occurrence or the magnitude of the effect. The changes in flame propagation rate resulting from these flame induced effects, however,

are smaller than those produced by a turbulent mixture flow so that a conservative estimate, where such effects are suspected, would be to estimate the equivalent turbulent flame propagation rate.

Unfortunately, a widely accepted theory of turbulent flame propagation does not exist and it has not clearly been established whether apparatus effects are involved in the measured values of turbulent flame propagation velocity. The principal measurements of turbulent flame velocity have involved the Bunsen burner technique with a turbulent gas flow. A turbulent flame velocity is computed in a manner analagous to the laminar burning velocity and serves as the burning rate coefficient. The turbulent flame velocity is a function of the same factors that affect burning velocity as well as the scale and intensity of the turbulence. Usually the data are presented in terms of the Reynolds number of the flowing mixture as illustrated in Figure 61 from Ref 65.

It is difficult to generalize the effects of turbulence but relationships of the form:

$$\frac{U_t}{U_f} \sim R_e^{1/4} \tag{80}$$

and (Ref 61)

$$\frac{U_t}{U_f} = a + b R_e \tag{81}$$

provide a reasonable method of estimation. Laboratory studies such as those illustrated in Figure 62 (Ref 66) show turbulent flame velocities of the order of 5 to 6 times the laminar burning velocity although ratios of U_t/U_f as high as 10 are not unreasonable. For hazard evaluation studies, a factor of 15 times laminar burning velocity appears as a reasonable estimate for the maximum burning rate of a free flame in a tube. This value would be increased by the effects of gas flow velocity as illustrated for the laminar flame, as well as flame area, and expansion ratio, , defined previously. Effects of fuel type, composition, pressure and temperature are, of course, already included in U_f.

The burning rate of a free flame is not a measure of the maximum gas flow rate which can pass through a stationary flame if obstacles exist in the flow. An elementary way of looking at supported flames is that some point of attachment, either in the boundary layer or recirculation zone adjacent to the obstacle, has a sufficiently low velocity to hold the flame. The flame surface then extends into the high velocity stream at an angle which limits the normal velocity component of flow through the flame to a value given by the laminar or turbulent burning velocity, whichever applies.

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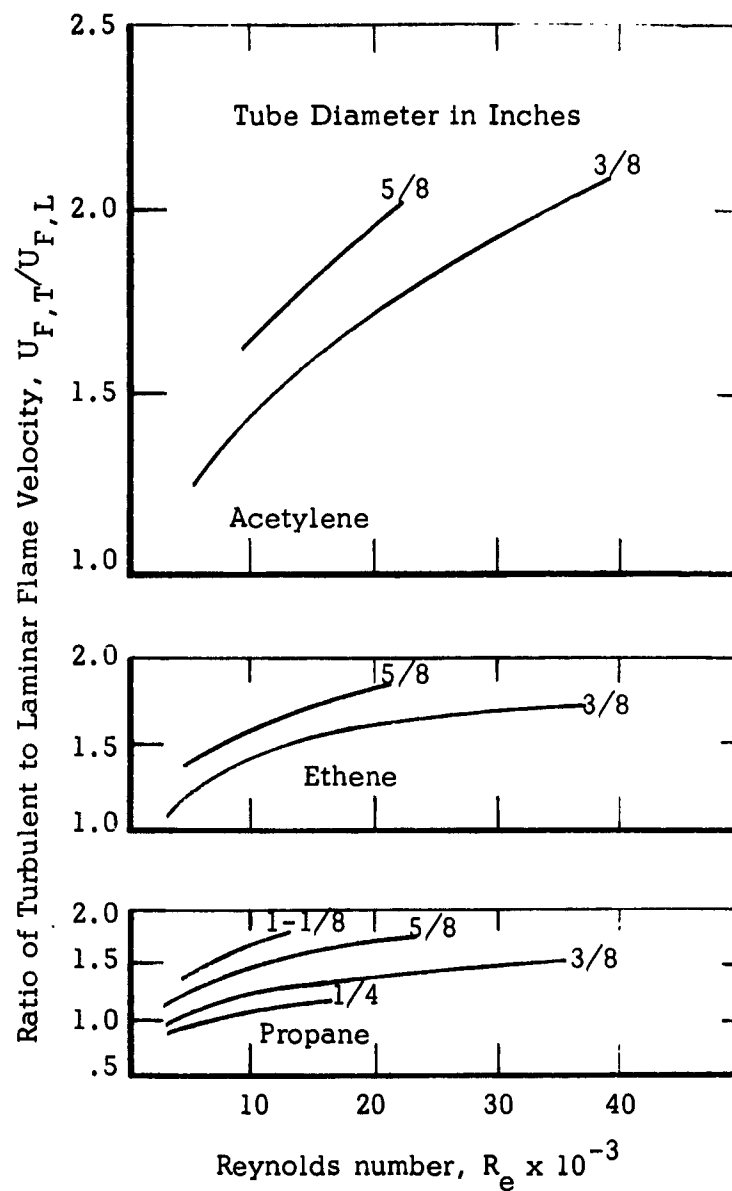
Figure 61. Effect of Reynolds Number on Ratio of Turbulent to Laminar Flame Velocity; Hydrocarbon-Air Flames; Constant Density and Viscosity

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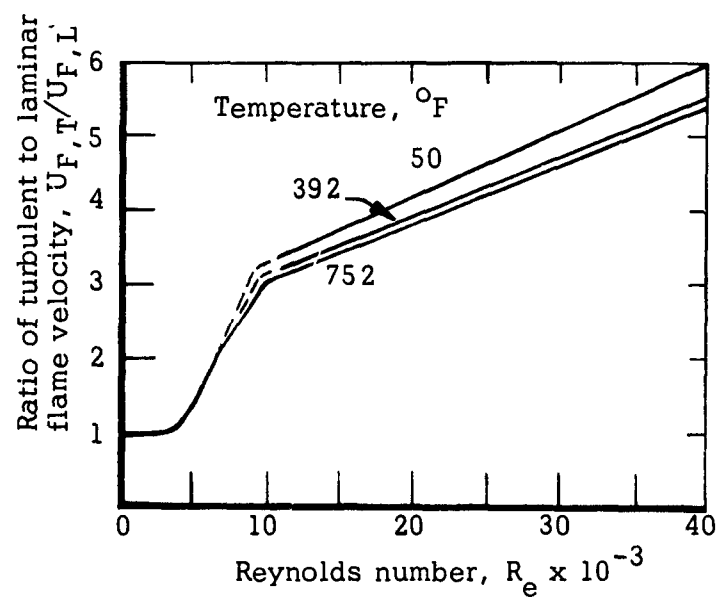
Figure 62. Effect of Reynolds Number on Ratio of Turbulent
to Laminar Flame Velocity

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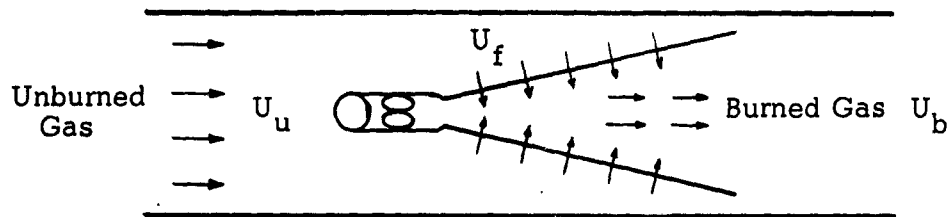
As illustrated, for an unburned gas velocity, U_u, the flame orients itself to the flow so that the normal component of the flow is of the order of U_f (or U_t). While this model over-simplifies the mechanism, it does describe a situation in which the stream velocity can be several hundred times greater than the flame velocity. As the flow velocity increases, the flame adjusts its shape to accommodate the greater flow until a point is reached where the flame blows off. The blow-off velocity, U_{bo}, is related to the size of the obstacle and is related to the obstacle dimension by:

$$U_{bo} \sim d^{1/2} \qquad \text{Laminar boundary layer} \qquad (82)$$

$$U_{bo} \sim d \qquad \text{Turbulent boundary layer} \qquad (83)$$

where U_{bo} = velocity at blow-off

   d   = critical dimension of obstacle

While the shape of the obstacle introduces some differences in blow-off velocity, shape is a secondary variable and can often be accounted for by suitable choice of the critical dimension, d.

For the situation where a large part of the cross-sectional area of the duct is blocked by the obstacle, one should use the local velocity at the location of the obstacle, given approximately by

$$U_o = U_u \frac{A_u}{A_o} \qquad (84)$$

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where (see below)

U_o = velocity past obstacle

U_u = approach velocity in duct

A_u = area of duct

A_o = open area near obstacle
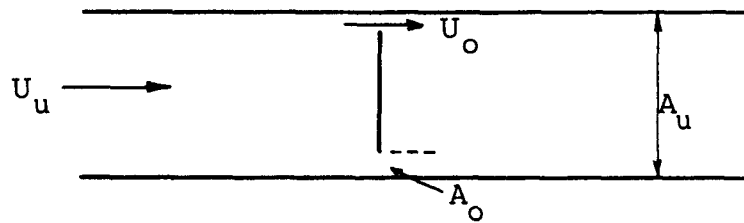
The blow-off velocity can be considered as the ratio of a critical length, L, and a critical time, Υ . It has been shown (Ref 67) that the relation

$$U_{bo} = \frac{L}{\Upsilon}$$ (85)

where L = length of recirculation zone

Υ = critical reaction time

can be used to describe blow-off velocity. The length of the recirculation zone, L, is determined by aerodynamic factors while the critical reaction time, Υ , is determined by the chemical reaction rate. Variation of blow-off velocity with temperature and pressure can thus be related to variation of L and   with these parameters. For constant Reynolds number, the variation of blow-off velocity may be expected to depend only on Υ which can be considered as the reciprocal of a reaction rate. Hence, one can write

$$\frac{U_{bo}}{L} \sim p^n \, e^{-E/RT}$$ (86)

where n = reaction order ~ 1.8 for hydrocarbon fuels

E = activation energy $\sim 72,000$ Btu/pound-mole for hydrocarbon fuels

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Another important factor relating flame propagation effects to fire and explosion hazards involves the blow-off and flash-back of flames at the open end of tubes such as vent lines. Such an unconfined flame, burning at the end of a tube and corresponding closely to a Bunsen burner type flame, will remain in a fixed position at the tube end only within certain ranges of velocity. If the mixture velocity through the tube is increased beyond a critical value, the flame will move away from the tube or blow-off. If the mixture velocity is decreased below a critical value the flame will move into the tube or flash back if the tube diameter is greater than the quenching distance or become extinguished if the tube diameter is less than the quenching distance.

The critical condition for both blow-off and flash-back of such unconfined flames is associated with the existence of a region within the flowing gas where the mixture velocity is equal to the burning velocity. This condition is generally found in the boundary layer near the wall of the tube since, under normal flow conditions, the velocity of the gas remote from the wall is greater than the local velocities in the boundary layer.

As the mixture velocity is increased, the velocity profile near the wall becomes steeper and the location of a zone where the mixture velocity is equal to the burning velocity moves closer to the wall until the quenching action of the wall prohibits flame propagation, and the remaining flame remote from the wall moves away from the burner. If one assumes a linear velocity profile near the tube wall with the stream velocity equal to zero at the wall, the velocity profile is given by

$$U = gd \tag{87}$$

where U = local stream velocity
  d = distance measured from wall
  g = constant, called boundary velocity gradient

There is associated with each flame a critical distance near a wall in which flame cannot exist. This distance, called the flame penetration distance (Ref 68) and denoted by d_{pen} is related to but not equal to the quenching distance. The penetration distance can be estimated by (Ref 69)

$$d_{pen,b} = \frac{1}{3} d_c \tag{88}$$

where d_c = cylindrical tube quenching distance

Using the concept of a penetration distance, there is then a critical value of the boundary velocity gradient, g_{cb}, which will make the product

$$g_{cb} d_{pen,b} = U_f \tag{89}$$

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A larger value of g_c implies a stream velocity greater than the burning velocity everywhere in the tube beyond the penetration distance and the flame will blow off.

As the mixture flow velocity is reduced, a critical condition is reached where the burning velocity exceeds the flow velocity within the tube and the flame flashes back into the tube. A critical boundary velocity gradient corresponding to a critical velocity also exists for flashback. The critical boundary velocity gradient for blow-off and flashback do not coincide, however, since the position of the flame with respect to the exit lip of the tube changes as the flow velocity changes. The quenching action of the wall is either decreased or increased depending upon the position of the flame. As the flow velocity is decreased, the flame moves closer to the tube and increased quenching is experienced so that a larger penetration distance is required to achieve the true normal burning velocity. For constant burning velocity an increase in d_{pen} requires a decrease in g_c to maintain a constant product. There is, therefore, a region of stream velocities and associated boundary velocity gradients for which the flame is stable. Above a critical value the flame blows off; below a critical value the flame flashes back.

A typical stability diagram is illustrated in Figure 63 (Ref 70) which includes the effect of mixture temperature. The data presented for propane-air flames would apply reasonably well to other hydrocarbon fuels. The change in blow-off and flashback velocity with temperature can be represented by the following equations (Ref 61):

$$U_{bo} = 100 + 4.5 \times 10^{-3} T^{1.9} \qquad (90)$$

$$U_{fb} = 100 + 1.15 \times 10^{-9} T^{4.2} \qquad (91)$$

The effect of pressure on flashback and blow-off velocities has not been as well established. If we examine the equation for boundary velocity gradient (Ref 71)

$$g = \frac{F_{fr} \rho U^2}{2u} = \frac{F_{fr} U R_e}{2d} \qquad (92)$$

where F_{fr} = friction factor

ρ = density

U = stream velocity

d = tube diameter

R_e = Reynolds number

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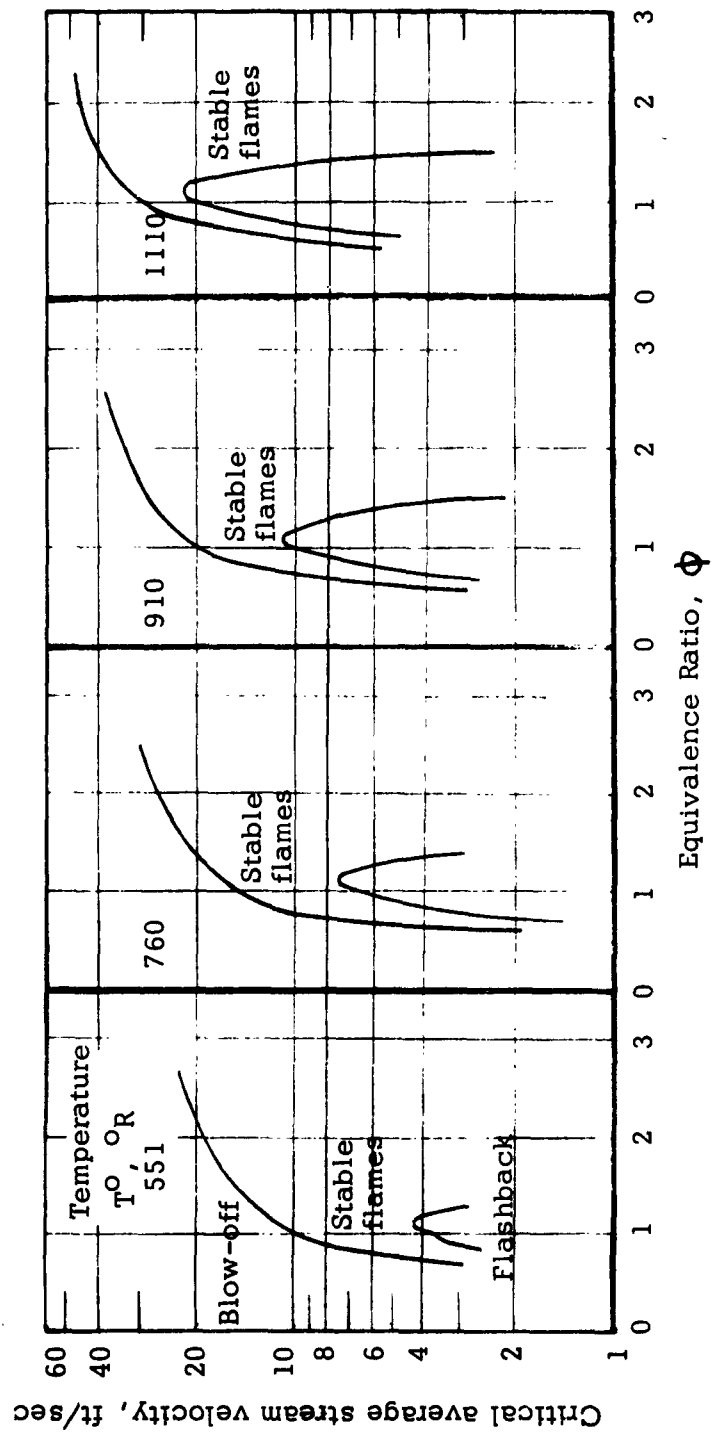
Figure 63. Effect of Initial Mixture Temperature on Stable Flame Region for Propane–Air Flames on 15.6–Millimeter Burner at Atmospheric Pressure

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then
$$U = \frac{2dg}{F_{fr}R_e} \tag{93}$$

At constant Reynolds number, U varies as g. Since

$$g = U_f/d_{pen} \sim \frac{3U_f}{d_c} \tag{94}$$

where U_f = burning velocity

d_c = cylindrical tube quenching distance

If we assume on the basis of previous discussion of the variation of burning velocity and quenching distance with pressure that:

$$U_f \sim P^0 \tag{95}$$

$$d_c \sim P^{-1} \tag{96}$$

$$U \sim g \sim P \tag{97}$$

The flame propagation characteristics of a completely confined flame are difficult to calculate. Extensive work has been done on the propagation of flame in a spherical bomb with a central source of ignition. Some estimate of the propagation of confined flames can be made on the basis of this work.

Consider ignition of a combustible mixture at the geometric center of a completely closed space of a given volume. In order to estimate the results of the flame propagation treat this volume in terms of a sphere of equal volume. Typical behavior of the pressure within the volume as a function of time and as a function of location of the flame are shown in Figure 64 and Figure 65 from data of Ref 68. It is evident that the pressure remains essentially constant near the initial pressure until the flame has progressed to a point about midway along the radius of the bomb. At this point the pressure rises rapidly to the thermodynamic equilibrium pressure for a constant volume explosion, P_e. To the point of rapid change in pressure, the rate of flame propagation can be calculated by equations (78) and (79) for an unconfined spherical flame. Beyond this point a more complicated equation is required.

The set of equations which describe such a spherical explosion with central ignition are (Ref 68)

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The y-axis is labeled $\frac{P}{P_e}$ with values 0, .2, .4, .6, .8, 1.0.

The x-axis is labeled $\frac{t}{t_e}$ with values .2, .4, .6, .8, 1.0.

Legend:

P_e = equilibrium end pressure

P = bomb pressure

t = time after ignition

t_e = time at end of propagation
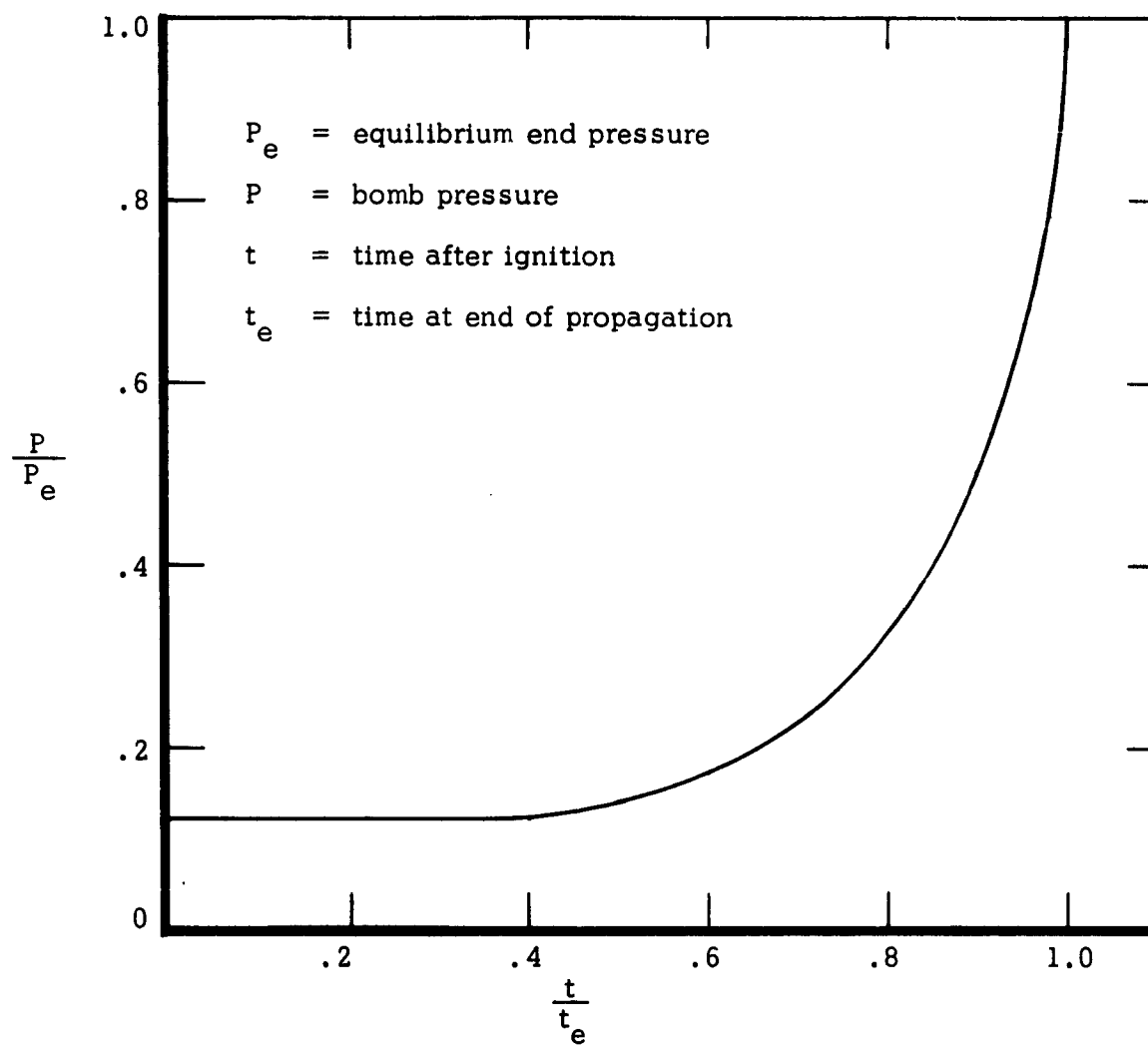
Figure 64. Pressure Rise in a Closed Bomb Explosion with Central Ignition; Pressure versus Time
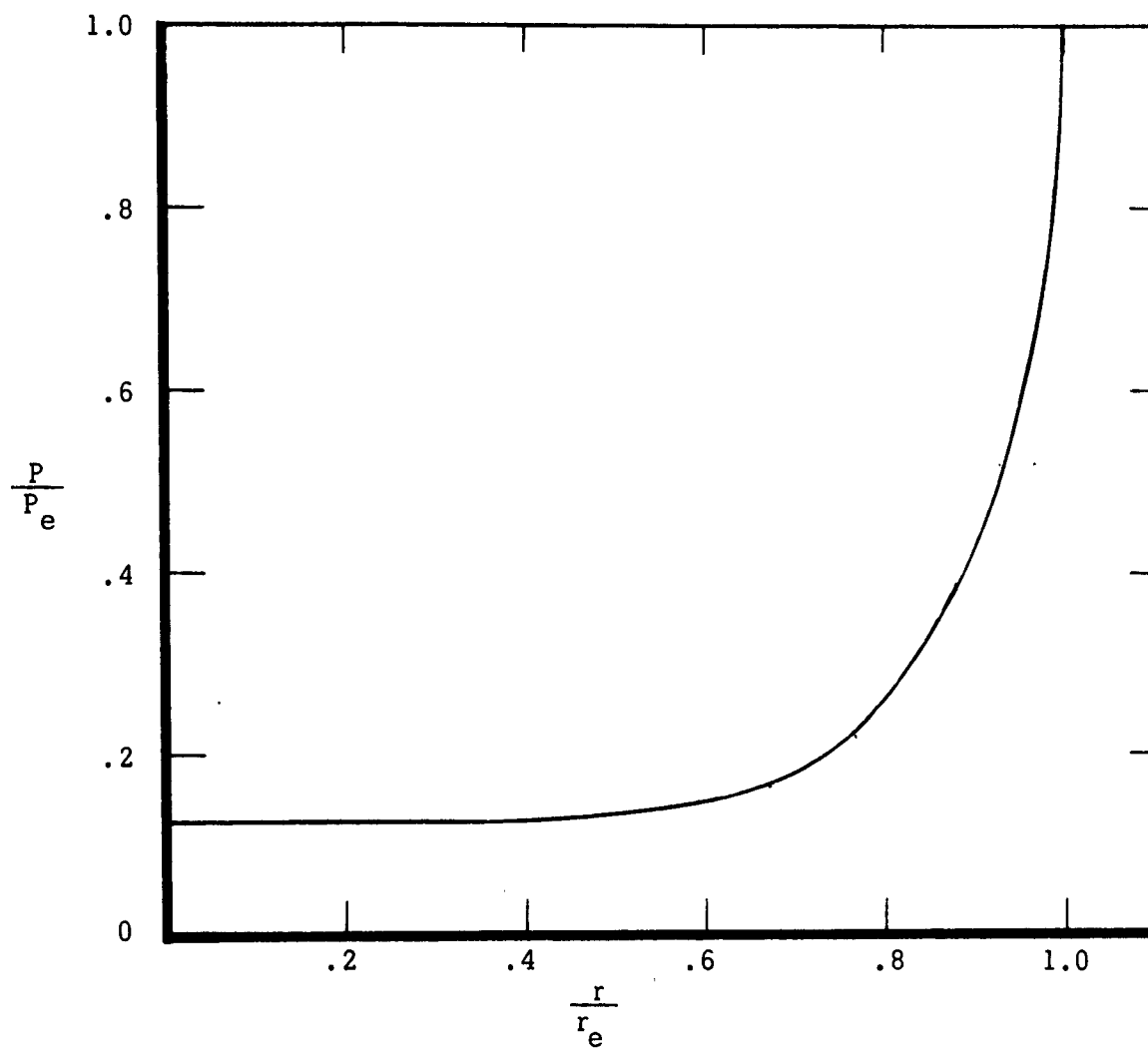
Figure 65. Pressure Rise in a Closed Bomb Explosion with
Central Ignition; Pressure versus Radius

$$\left(\frac{r_i}{r_e}\right)^3 = \left(\frac{P - P_i}{P_e - P_i}\right) \tag{98}$$

$$\left(\frac{r_b}{r_e}\right)^3 = \left[1 - \left(\frac{P_i}{P}\right)\left(\frac{T_u}{T_i}\right)\left(\frac{P_e - P}{P_e - P_i}\right)\right] \tag{99}$$

$$\frac{T_u}{T_i} = \left(\frac{P}{P_i}\right)^{\frac{\gamma-1}{\gamma}} \tag{100}$$

$$U_f = \frac{dr_i}{dt}\left(\frac{r_i}{r_b}\right)^2 \left(\frac{P_i}{P}\right)^{1/\gamma} \tag{101}$$

where r_i = radius inside flame shell

r_e = radius of bomb

P = pressure in bomb

P_i = initial pressure

P_e = final equilibrium pressure

T_u = temperature of unburned gas in bomb

T_i = initial temperature of mixture

t = time

γ = specific heat ratio of unburned gas

U_f = burning velocity

Assuming that the burning velocity of the mixture is known, there are five unknowns, r_i, r_b, P, T_u, dr_i/dt and only four equations. A fifth equation may be introduced by relating r_i and r_b through the expansion ratio used for an unconfined spherical flame so that

$$\left(\frac{r_i}{r_b}\right)^3 = \quad = \frac{\rho_i}{\rho_b} \tag{102}$$

where ρ = gas density

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From the complete set of equations it is possible to solve for the pressure in the container, P, which varies from P_i to P_e and the velocity of flame propagation:

$$U = \frac{dr_b}{dt} \tag{103}$$

The environment of the supersonic transport introduces no new variations into the problem. A low value of P_i limits the maximum pressure, P_e. This maximum pressure is calculated from thermodynamic equilibrium and does not involve the above equations which determine only how fast the maximum pressure is achieved. The high temperature environment is reflected principally in producing a high value of U_f which increase the rate of pressure rise, and will also affect the maximum pressure in the thermodynamic calculations.

In a hazard analysis, the maximum pressure is, of course, a measure of the force which the chamber must withstand. The rate of pressure rise, however, is also of significance. The fact that the pressure rise does not become rapid until r/r_e is about 1/2 or about 1/8 of the mixture is consumed means that detection of such an explosion based on pressure rise will lag considerably behind the actual initiation and appearance of the flame. The damage produced by an explosion will also depend, at least in part, on whether the container ruptures before maximum pressure is achieved. If the bay or chamber is vented by failure of a wall early in the process, the violence of the explosion and damage potential of shrapnel will be much less than if the failure occurs at higher pressure. Ideally, therefore, if blow-out patches are used these should operate at the lowest pressure possible without introducing a reliability problem by the possibility of accidental rupture during normal pressure transients.

The previous discussion has considered a spherical container with central ignition. If the container has a different shape or if ignition is not centrally located, the rate of pressure rise will differ from the ideal case but the maximum pressure rise should be the same.

9. Detection and Extinction of Flames

The fundamental problem of fire detection and extinction is not very different from the problems associated with subsonic aircraft. A few differences do exist, however. These areas will be discussed in this section along with a brief summary of the status of halogenated hydrocarbon extinguishants.

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The problem of detection of flames is complicated by the fact that three different types of combustion phenomena are involved:

     a. Oxidation
     b. Cool Flames
     c. Normal Flames

Detection of the oxidation process cannot be accomplished by the usual spectroscopic techniques since the emission of useful frequencies does not occur. Two methods of detection are possible, neither particularly practical or reliable. The principal changes which would serve as the object of the detection system are changes in temperature and composition. The changes in temperature are small and could be quite localized so that this method, while theoretically possible, would be difficult to use. Changes in composition, formation of peroxides, etc. could be detected by various sensors including gas chromatographs, thermal conductivity cells and other instrumental methods of chemical analysis. Diffusion of species makes such a detection method less localized but quite slow compared to spectroscopic methods. While it would be desirable to detect oxidation as a means of predicting more serious hazards, no fully satisfactory method can be suggested at this time.

Cool flame detection is considerably easier with conventional techniques. Spectroscopic techniques could be developed to detect the characteristic emission from cool flames and, in fact, differentiate cool flames from normal flames. The characteristic emission from cool flames is due to formaldehyde instead of the C_2, CH and OH emission found in normal flames (Ref 72). The formaldehyde emission which occurs in the temperature range from about 400°F to 750°F is classed as chemiluminescence rather than thermal emission and would be readily distinguished from background radiation.

The detection of normal flames presents only one problem which differs from subsonic aircraft. The high temperature environment causes an increase in the background infra-red radiation. Care would have to be taken that infra-red sensors did not operate in the range of frequencies emitted by the hot surfaces. Ultra violet sensors would have no new interference problems and could be used in the conventional manner. A graph of flux density versus wavelength for black bodies at various temperatures is given in Figure 66 (Ref 73).

The most widely considered extinguishants for aircraft use are halogenated hydrocarbons. These extinguishants are also considered for supersonic transport applications.

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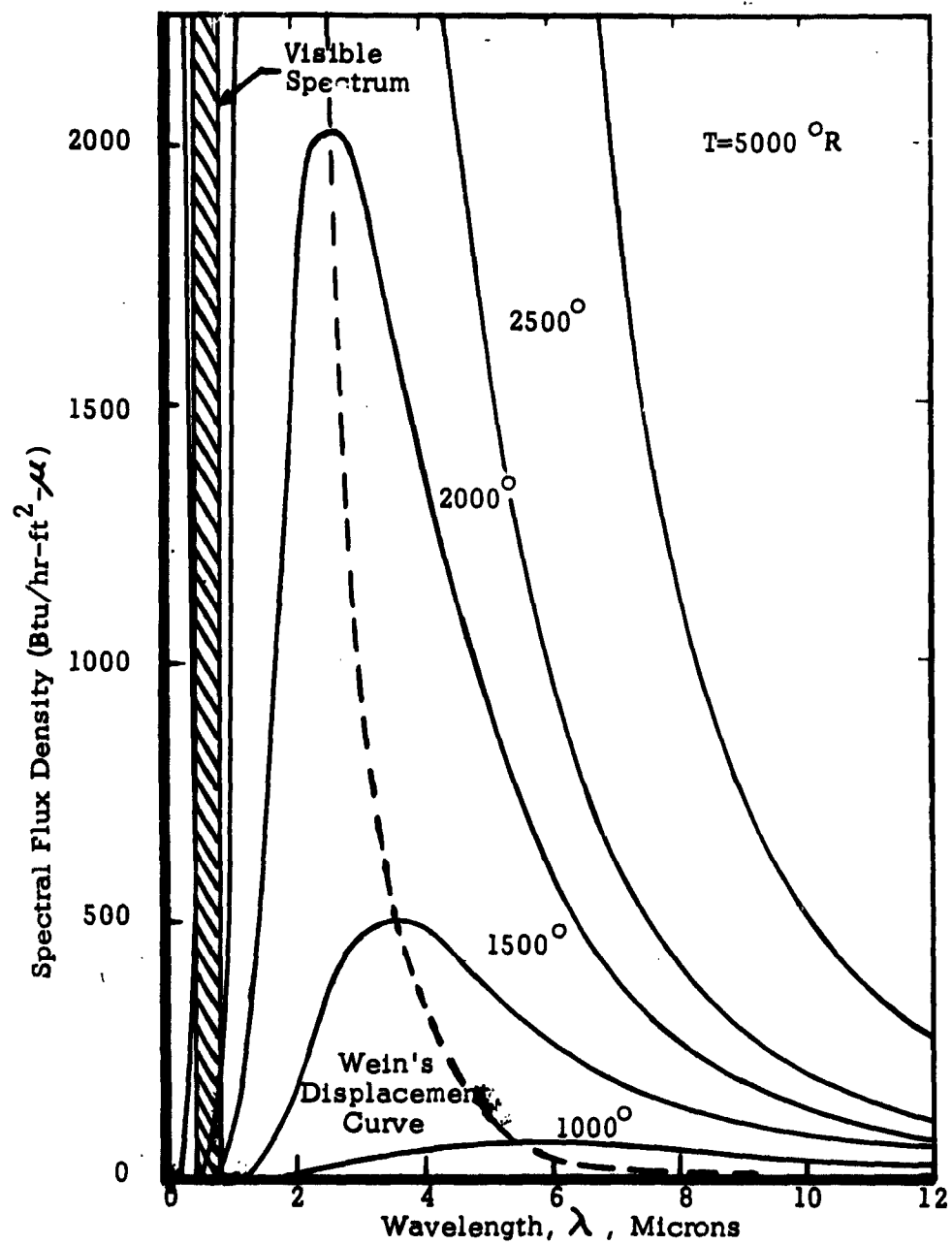
Figure 66. Energy Distribution for a Black Body

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Extinguishing agents are effective in quenching a flame as a result of a combination of several possible effects. The agent may cool the reaction and surroundings below a level of temperature which can support a flame; the agent may act as a barrier between the fuel and air, and the agent may inhibit the chemical reactions supporting the flame. Of these, the chemical inhibition has been the most widely investigated factor in the selection of extinguishing agents. The first two factors are heavily dependent on the quantity and mode of application of the agent and, in a sense, less dependent on the chemical nature of the agent although heat capacity, volatility and physical characteristics are involved.

The inhibition of flames by various agents has been studied principally by determining the effect of such agents on the ignition, flammability and burning velocity of various fuel-air mixtures. Of these, the effect of various agents on flammability limits has been the most widely used. The quantity of agent in a homogeneous fuel-air-agent mixture which prevents flame propagation, not only permits relative comparison of the inhibition efficiency of various agents but also defines the quantity of agent necessary to inert a given space under specified environmental conditions of temperature and pressure.

A typical flammability limit versus pressure curve is illustrated in Figure 67 (Ref 74) for a propane-air mixture and the same mixture containing 0.5 volume percent methyl bromide. Methyl bromide addition serves to reduce the flammable range at all pressure levels. Although there is some difference in the quantitative effect of methyl bromide at different pressure levels, a reasonable comparison between various agents can be made on the basis of tests at a single pressure level, usually atmospheric pressure.

Increasing the quantity of agents causes further reductions in the flammable area until a critical quantity of agent has been added which prevents flame propagation in all possible fuel-air concentrations. The change in flammability with agent concentration at one atmosphere pressure is illustrated in Figure 68 (Ref 75) for gasoline-air mixtures. The maxima represent the quantity of agent required to prevent flame propagation in all mixtures of the specified fuel with air. The comparative effects of numerous halogenated hydrocarbon agents on n-heptane-air flammability has been reported in Ref 76 and are summarized in Table 31. In the table, the peak fuel concentration refers to the volume percent fuel in the fuel-air-agent mixture at which the maximum agent concentration is required, the peak agent concentration refers to the volume percent agent in the mixture at the maximum. The third column in the table gives the fuel-air mixture composition exclusive of agent at the maximum.

These measures of extinguishing agent effectiveness apply to normal flames. It has been suggested that the action of an extinguishing agent involves decomposition of the agent to produce products which trap free

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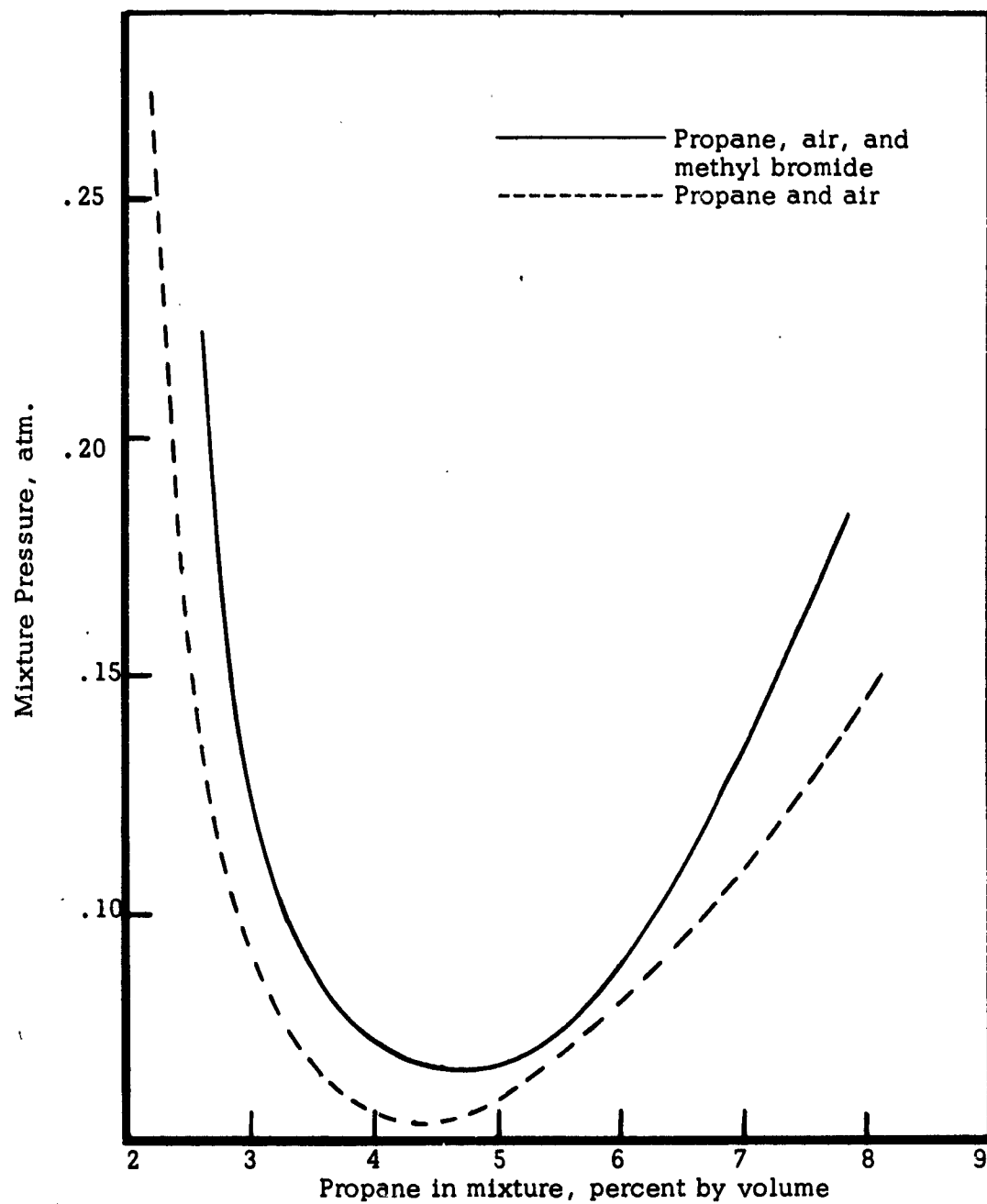
Figure 67. Effects of Additives on Low Pressure Limits of Flame
Propagation in Propane-Air Mixtures in 3.73-Centimeter-
Diameter Tube

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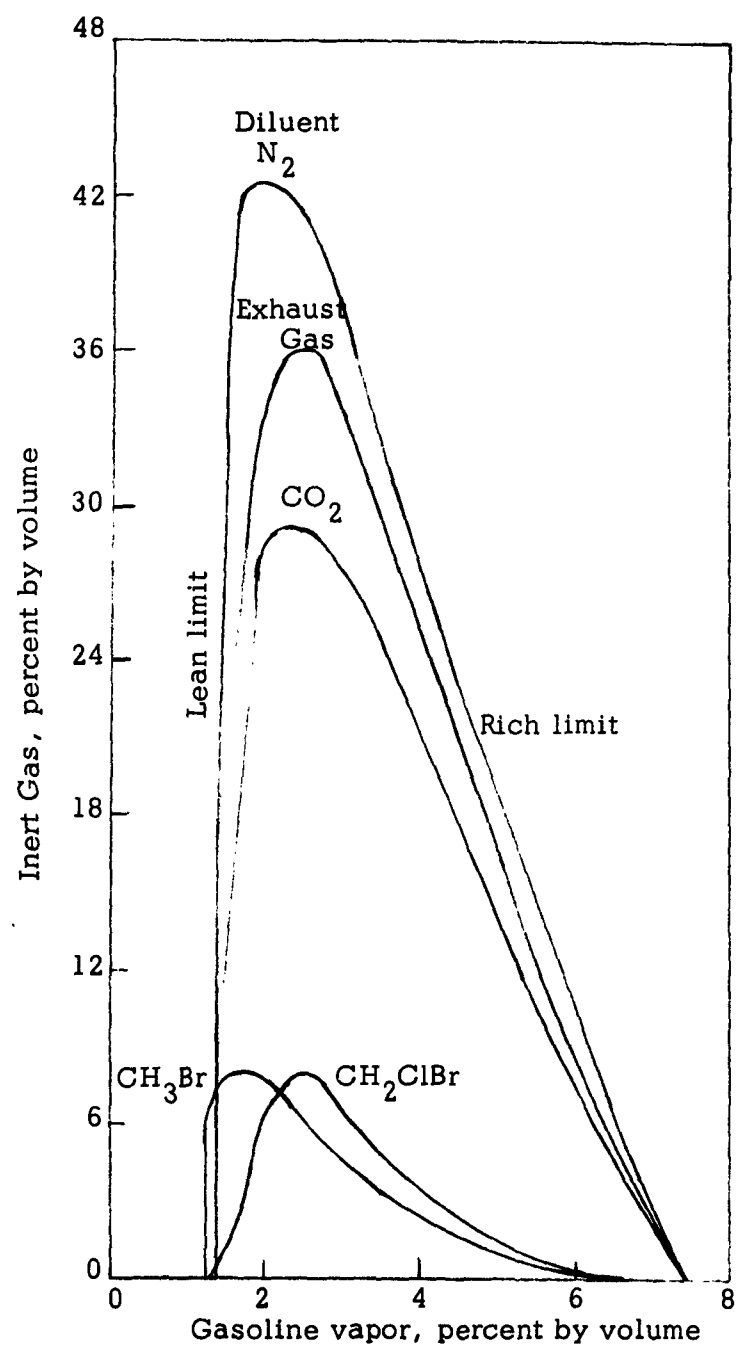
Figure 68. Effect of Diluents on Flammability Limits of Gasoline

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Table 31. Flammability Peaks of n-Heptane-Agent-Air Mixtures

Agent	Peak fuel concentration, percent by volume	Peak agent concentration, percent by volume	Peak Fuel concentration (Fuel and air only) % by volume	Fuel equivalent of agent
CBr_2F_2	4.4	4.2	4.6	0.55
CBr_3F	3.0	4.3	3.1	.91
$CBrF_2CH_2Br$	3.4	4.3	3.6	.77
$CBrF_2CBrClF$	3.5	4.6	3.7	.70
$CF_3CHBrCH_3$	3.5	4.9	3.7	.65
$CBrF_2CBrF_2$	3.3	4.9	3.5	.69
CF_2ICF_2I	3.5	5.0	3.7	.64
CH_2Br_2	2.1	5.2	2.2	.92
CF_3CF_2I	3.0	5.3	3.2	.70
$CF_3CH_2CH_2Br$	1.5	5.4	1.6	1.02
CH_3CH_2I	2.3	5.6	2.4	.82
CF_3CBrF_2	4.0	6.1	4.3	.43
CH_3I	2.1	6.1	2.2	.79
$CBrF_3$	3.0	6.1	3.2	.61
CH_3CH_2Br	2.3	6.2	2.5	.73
$CH_2BrCF_2CH_3$	2.3	6.3	2.5	.71
$CClF_2CHBrCH_3$	1.5	6.4	1.6	.86
$CHBr_2F$	3.4	6.4	3.6	.52
CF_3CH_2Br	3.4	6.8	3.7	.47

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Table 31. continued Flammability Peaks of n-Heptane-Agent-Air Mixtures

Agent	Peak fuel concentration, percent by volume	Peak agent concentration, percent by volume	Peak fuel concentration (fuel and air only) % by volume	Fuel equivalent of agent
$C_6F_{11}C_2F_5$	3.4	6.8	3.7	.47
$1,3-C_6F_{10}(CF_3)_2$	3.4	6.8	3.7	.47
CF_3I	2.5	6.8	2.7	.63
$1,4-C_6F_{10}(CF_3)_2$	3.4	6.8	3.7	.47
CH_2BrCH_2Cl	1.7	7.2	1.8	.72
$CClF_2CH_2Br$	3.0	7.2	3.2	.51
$C_6F_{11}CF_3$	3.0	7.5	3.2	0.49
C_7F_{16}	3.0	7.5	3.2	.49
CH_2BrCl	2.2	7.6	2.4	.61
$CHBrF_2$	4.0	8.4	4.4	.30
$CClF_2CCl_2F$	4.0	9.0	4.4	.28
$CBrClF_2$	3.0	9.3	3.3	.39
CH_3Br	1.4	9.7	1.6	.57
$CF_2 CHBr$	2.6	9.7	2.9	.42
C_4F_{10}	3.4	9.8	3.8	.32
$CClF_2CClF_2$	3.0	10.8	3.4	.38
CCl_4	3.2	11.5	3.6	.29
$CF_3CHClCH_3$	1.0	12.0	1.1	.50
$CF_3CH_2CH_2Cl$	.7	12.2	.8	.52

Table 31. concluded Flammability Peaks of n-Heptane-Agent-Air Mixtures

Agent	Peak fuel concentration, percent by volume	Peak agent concentration, percent by volume	Peak fuel concentration (fuel and air only) % by volume	Fuel equivalent of agent
$CClF_3$	3.3	12.3	3.8	.25
CF_3CF_3	3.0	13.4	3.5	.25
CCl_2F_2	3.9	14.9	4.6	.15
$CHCl_3$	3.6	17.5	4.4	.14
CHF_3	2.5	17.8	3.0	.22
$CHClF_2$	2.3	17.9	2.8	.24
C_4F_8	2.3	18.1	2.8	.23
CF_4	1.8	26.0	2.4	.18

radicals and atoms and inhibit the normal flame reactions. The temperature rise in cool flames is not sufficient to decompose the agent and hence the halogenated hydrocarbons are not particularly effective for the inhibition of cool flames. Metal alkyls such as tetraethyl lead, carbonyls such as iron carbonyl and certain amines are more effective for cool flame inhibition. These have been discussed in the section dealing with cool flame ignition.

The desirable properties of an agent suitable for supersonic transport applications have been identified in Ref 77 as:

a. Suitable for use in combating hydrocarbon and electrical fires. The weight effectiveness of the agent shall be preferably comparable to presently utilized halogenated hydrocarbons.

b. No more toxic than methyl bromide.

c. Suitable for use at -65°F to temperatures approaching 500°F.

d. Shall be stable in storage under recurring anticipated supersonic transport flight conditions as well as ground climatic conditions for up to three years.

e. Capable of production at reasonable cost and with existing production facilities.

f. No more corrosive than bromochloromethane.

g. Shall be a nonconductor of electricity.

h. Shall have suitable pressure-temperature characteristics making the agent utilizable in a low rate discharge system. This assumes a total system pressure of 400 psia (nitrogen plus agent) at 70°F. System pressure for the purpose of this investigation at 500°F should not exceed a maximum of 1660 psia. This specification is selected so that present agent containers might be utilized. It is subject to change if system analysis shows a high rate discharge system and higher pressures are more desirable. Low temperature volatility and viscosity of the agent should approach those of chlorobromomethane for effective discharge at -65°F.

The agents listed in Table 31 do not meet these requirements principally with regard to high temperature vapor pressure and thermal stability. Of the agents listed in Table 31, CH_2BrCl, CBr_2F_2, $CBrClF_2$, $CBrF_3$ have been utilized in current aircraft. The physical properties of three of these are illustrated in Table 32. The vapor pressures of $CBrClF_2$ and $CBrF_3$ are excessive at 500°F while CBr_2F_2 has a thermal stability limit at 350°F, and CH_2BrCl at 250°F (Ref 77).

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Table 32. Properties of Current Extinguishants

Compound	MW	BP°F	FP°F	Density 77°F	Critical Temp. °F	Critical Pressure (psia)	Thermal Stability Limit °F	$\Delta H_{vap.}$ K-Cal/Mole	Exting. Pressure 500°F (psia)	System Pressure 500°F (psia)*
CF_3Br	149	-72	-282	1.57	154	574	500	4.20	2725	3450
$CBfClF_2$	165	25	-257	1.83	309	565	400	5.29	2100	2760
CF_2Br_2	210	73	-223	2.28	390	593	350	5.93	1160	1860

* Assumes system pressure of 400 psia at 70°F

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A study of halogenated hydrocarbons with higher thermal stability and lower vapor pressure is reported in Ref 77. A list of candidate extinguishing agents is given in Table 33 and their relative rating in Table 34. Vapor pressures for possible candidate extinguishants and some currently used agents are shown in Figure 69 (Ref 77) as a function of temperature and viscosities are illustrated in Figure 70 (Ref 77) as a function of temperature.

One of the major problems associated with consideration of extinguishants for supersonic transport applications is the high pressure which may result in the storage system at high temperature due to the vapor pressure of the agent. The storage system usually involves a pressurizing gas to provide adequate spray capability at low ambient temperature where the agent vapor pressure is low.

At any temperature the total pressure is given by

$$P_t = P_g + P_e \tag{104}$$

where P_t = total pressure

P_g = pressurizing gas pressure

P_e = agent vapor pressure

The vapor pressure of the extinguishant can be obtained from data such as that presented in Figure 69 or calculated from equations such as equation (13). As a reasonably accurate estimate, the vapor pressure of the agent will depend only on temperature and not on the fill ratio, driver gas pressure or size of system.

The pressure of the driver gas (often nitrogen) can be obtained from initial fill conditions of the system. If the initial conditions of the storage system are:

V_t = total volume of system

V_e = volume of extinguishant

$V_t - V_e$ = volume of pressurizing gas

$V_R = \dfrac{V_e}{V_t}$ = fill ratio

then the pressure of the driver gas added initially is either established at the time of filling or can be obtained from the relationship

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Table 33. Properties of Candidate Extinguishants

Compound	Molecular Weight	Boiling Point °F	Freezing Point °F	Density 77°F	Critical Temp. °F	Critical Pressure (psia)	Thermal Stability Limit °F	ΔH vap. K-Cal/Mole	Specific Heat-Liquid Cal/Deg-Gm	Exting. Pressure 500°F (psia)*	System Pressure 500°F (psia)**	Exting. Capability. Wt/100 l Heptane-Air CB = 43.9 g
1 $H(CF_2)_2CH_2Cl$	150.5	133	-112	1.199	480	970	550	6.90	0.61	1080(4.8)	1790	82.6
2 $CFCl_2CHCl_2$	186	102	-112	1.622	433	840	375	7.24	0.55	1140(5.0)	1850	36.6
3 $H(CF_2)_2CH_2Br$	195	163	-112	1.631	527	1080	475	7.79	0.54	680(2.4)	1400	45.3
4 $CF_3CBrClH$	197.5	126	-112	1.870	469	928	400	7.03	0.42	1025(4.5)	1735	30.7
5 $CF_2BrCFBrH$	242	169	-112	2.274	540	1260	350	7.60	0.38	720(1.8)	1440	36.8
6 $H(CF_2)_4CH_2Cl$	250.5	221	-112	1.325	618	815	550	8.38	0.58	200(0)	925	104.2
7 $CCl_3CF_2CFCl_2$	270.5	309	-121	1.779	757	290	500	8.94	0.60	990(0)	815	78.5
8 $CF_2BrCFBrCl$	276.5	194	-99	1.428	577	1085	375	8.36	0.38	500(0)	1225	55.5
9 $H(CF_2)_4CH_2Br$	295	245	-112	1.883	656	970	550	9.27	0.49	300(0)	1025	99.0
10 $CF_2BrCFClCF_2CFClH$	314	279	-112	1.950	710	540	525	10.71	0.46	250(0)	975	51.8

* Figures in parentheses are extinguishant vapor pressures at 70°F (psia)
** Assumes system pressure of 400 psia at 70°F

Nomenclature of Above Compounds

1) 1-Chloro-2,2,3,3-tetrafluoropropane
2) 1,1,2,2-Tetrachloro-1-fluoroethane
3) 1-Bromo-2,2,3,3-tetrafluoropropane
4) 1-Bromo-1-chloro-2,2,2-trifluoroethane
5) 1,2-Dibromo-1,1,2-trifluoroethane
6) 1-Chloro-2,2,3,4,4,5,5-octafluoropentane
7) 1,1,1,3-Pentachloro-trifluoropropane
8) 1,2-Dibromo-1-chlorotrifluoroethane
9) 1-Bromo-2,2,3,4,4,5,5-octafluoropentane
10) 1-Bromo-2,4-dichloro-1,1,2,3,4-hexafluorobutane

Table 34. Ranking of Candidate Extinguishants by Properties

Compound	Increasing Boiling Point	Freezing Point	Increasing Viscosity (-65°F)	Decreasing Density	Decreasing Critical Temperature	Decreasing Specific Heat	Decreasing Thermal Stability	Increasing Extinguishant Pressure 500°F	Increasing System Pressure 500°F	Extinguishant Effect Weight Basis	Extinguishant Effect Volume Basis	Total (Unweighted)
$H(CF_2)_2CH_2Cl$	3		2	10	8	1	1	8	8	8	9	63
$HCCl_2CFCl_2$	1	all	1	7	10	4	7	9	10	2	2	60
$H(CF_2)_2CH_2Br$	4	approx	8	6	7	5	5	6	6	4	4	58
$CF_3CBrClH$	2		3	4	9	8	6	8	9	1	1	57
$CF_2BrCFBrH$	5	same	4	1	6	10	8	7	7	3	5	57
$H(CF_2)_4CH_2Cl$	7		7	9	4	3	1	2	2	10	10	63
$CCl_3CF_2CFCl_2$	10		9	5	1	2	4	1	1	7	7	57
$CF_2BrCFBrCl$	6		6	8	5	9	7	5	5	6	6	65
$H(CF_2)_4CH_2Br$	8		5	3	3	6	2	4	4	9	8	56
$CF_2BrCFClCF_2CFClH$	9		10	2	2	7	3	3	3	5	3	56

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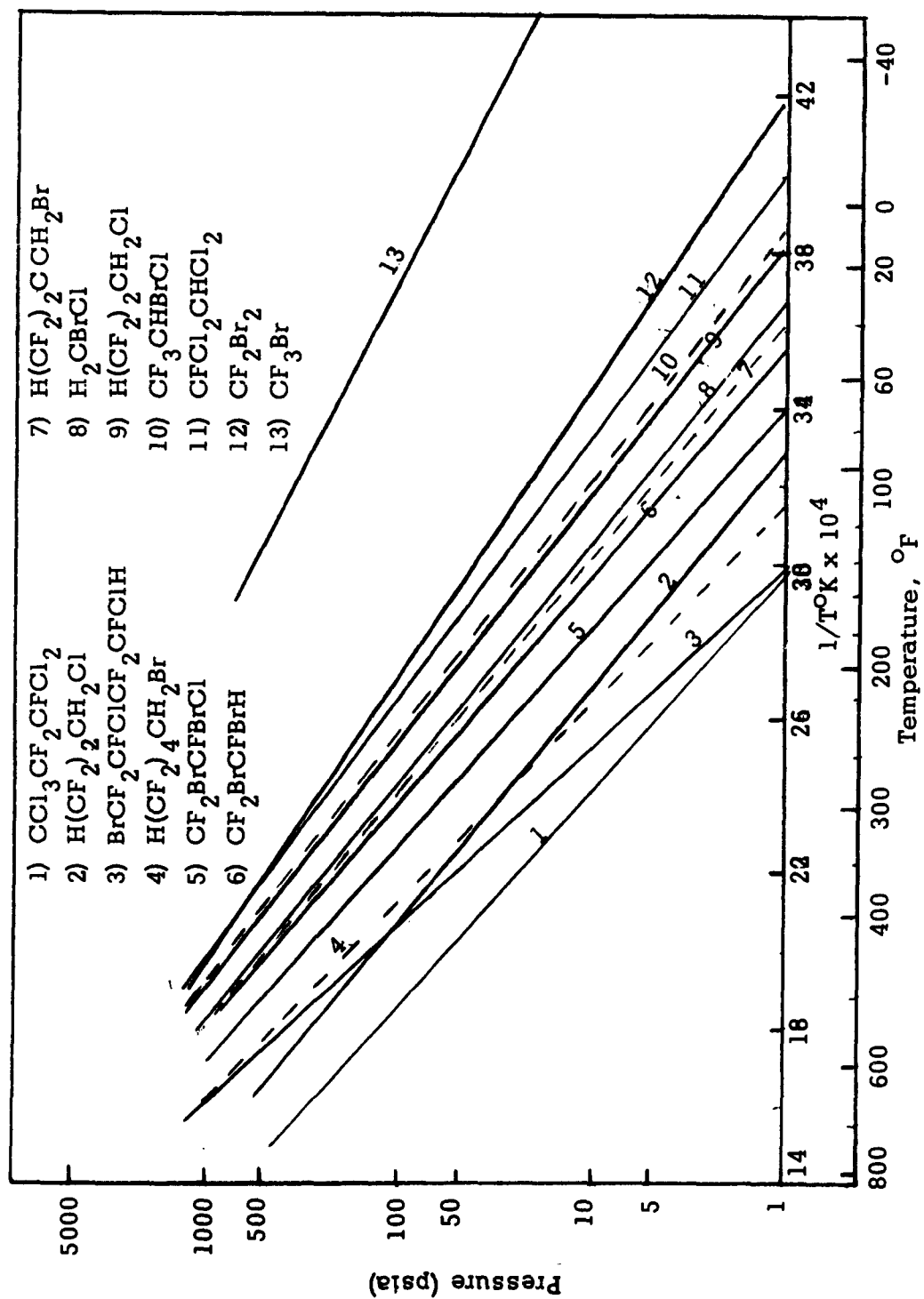
Figure 69. Vapor Pressure Curves of Agents

1) $CCl_3CF_2CFCl_2$
2) $H(CF_2)_2CH_2Cl$
3) $BrCF_2CFClCF_2CFClH$
4) $H(CF_2)_4CH_2Br$
5) $CF_2BrCFBrCl$
6) $CF_2BrCFBrH$
7) $H(CF_2)_2CCH_2Br$
8) H_2CBrCl
9) $H(CF_2)_2CH_2Cl$
10) $CF_3CHBrCl$
11) $CFCl_2CHCl_2$
12) CF_2Br_2
13) CF_3Br

1) $CBrF_3$
2) CH_3Br
3) $BrClCF_2$
4) CF_2Br_2
5) CH_2BrCl
6) $CFCl_2CHCl_2$
7) $CF_3CBrClH$
8) $H(CF_2)_2CH_2Cl$
9) $CF_2ClCFClCF_3$
10) CCl_4
11) $CF_2BrCFBrH$
12) $CF_2BrCFBrCl$
13) $H(CF_2)_2CCH_2Br$
14) $H(CF_2)_2CH_2Br$
15) $H(CF_2)_4CH_2Cl$
16) $CF_2BrCFClCF_2CHFCl$
17) $CCl_3CF_2CFCl_2$
18) $CF_2BrCClFCH_2CH_2Br$
19) $CF_2BrCFClCHClCH_2Cl$
20) $(HCF_2CF_2CH_2O)_3PO$

Figure 70. Viscosities of Candidate Extinguishants

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$$P_g = \frac{mRT}{M(V_t - V_e)} = \frac{m\,RTV_t}{M(1-V_R)} \tag{105}$$

where   m   = mass of driver gas

M   = molecular weight of driver gas

if the weight of gas rather than the pressure is given. In current systems, the extinguishant system is usually filled with pressurizing gas to give a pressure of 400 psia at 70°F, so that the initial value of P_g is given by

$$P_{g,i} = 400 - P_{e,i} \tag{106}$$

where $P_{g,i}$ = initial pressure of driver gas, psia

$P_{e,i}$ = vapor pressure of extinguishant at 70°F

At a fixed level of temperature within the storage system the total pressure will change as agent is used due to changes in the fill ratio, V_R. This change is given by:

$$P_t = P_e + P_{g,i} \left(\frac{V_{g,i}}{V_g} \right) \tag{107}$$

$$P_t = P_e + P_{g,i} \left(\frac{(V_t - V_e)_i}{(V_t - V_e)} \right) \tag{108}$$

$$P_t = P_e + P_{g,i} \left(\frac{(1 - V_R)_i}{(1 - V_R)} \right) \tag{109}$$

At a fixed fill ratio, the total pressure within the storage system can be calculated by assuming that the pressurizing gas behaves as a perfect gas and is insoluble in the extinguishant. This results in an equation of the form:

$$P_{t,T} = P_{e,T} + P_{g,70} \times \frac{T}{530} \tag{110}$$

where   T   = temperature, °R

If a change in liquid volume occurs due to expansion (or contraction) then the relationship:

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$$P_{t,T} = P_{e,T} + P_{g,70} \left(\frac{T}{530}\right) \left(\frac{V_{g,70}}{V_{g,t}}\right) \tag{111}$$

where $V_{g,70}$ = gas volume at $70^{\circ}F$ ($530^{\circ}R$)

$V_{g,T}$ = gas volume at T

Typical variations of extinguishant container pressure as a function of temperature for CF_3Br pressurized with nitrogen are illustrated in Figure 71. Equation (110) applies to the data below the critical point. For example, if the initial conditions are:

$P_{t,70}$ = 1015 psia (1000 psig)

$P_{e,70}$ = 205 psia (from vapor pressure curve)

$P_{g,70}$ = 810 psia

at $120^{\circ}F$ ($580^{\circ}R$):

$P_{e,120}$ = 395 psia (from vapor pressure curve)

$P_{g,120} = 810 \times \dfrac{580}{530} = 880$ psia

$P_{t,120}$ = 1275 psia = 1250 psig

These calculations have neglected the change in liquid volume with temperature due to expansion (or contraction) and vaporization (or condensation) of the liquid agent. The volume of liquid extinguishant at any temperature can be obtained from:

$$V_{e,T} = \frac{\rho_{e,70} V_{e,70}}{\rho_{e,T}} \tag{112}$$

where $V_{e,T}$ = volume at temperature $T^{\circ}F$

$V_{e,70}$ = volume at $70^{\circ}F$

$\rho_{e,70}$ = density at $70^{\circ}F$

$\rho_{e,T}$ = density at $T^{\circ}F$

The change of volume of liquid agent due to vaporization (or condensation) of part of the agent as a result of changes in vapor pressure with temperature is given by:

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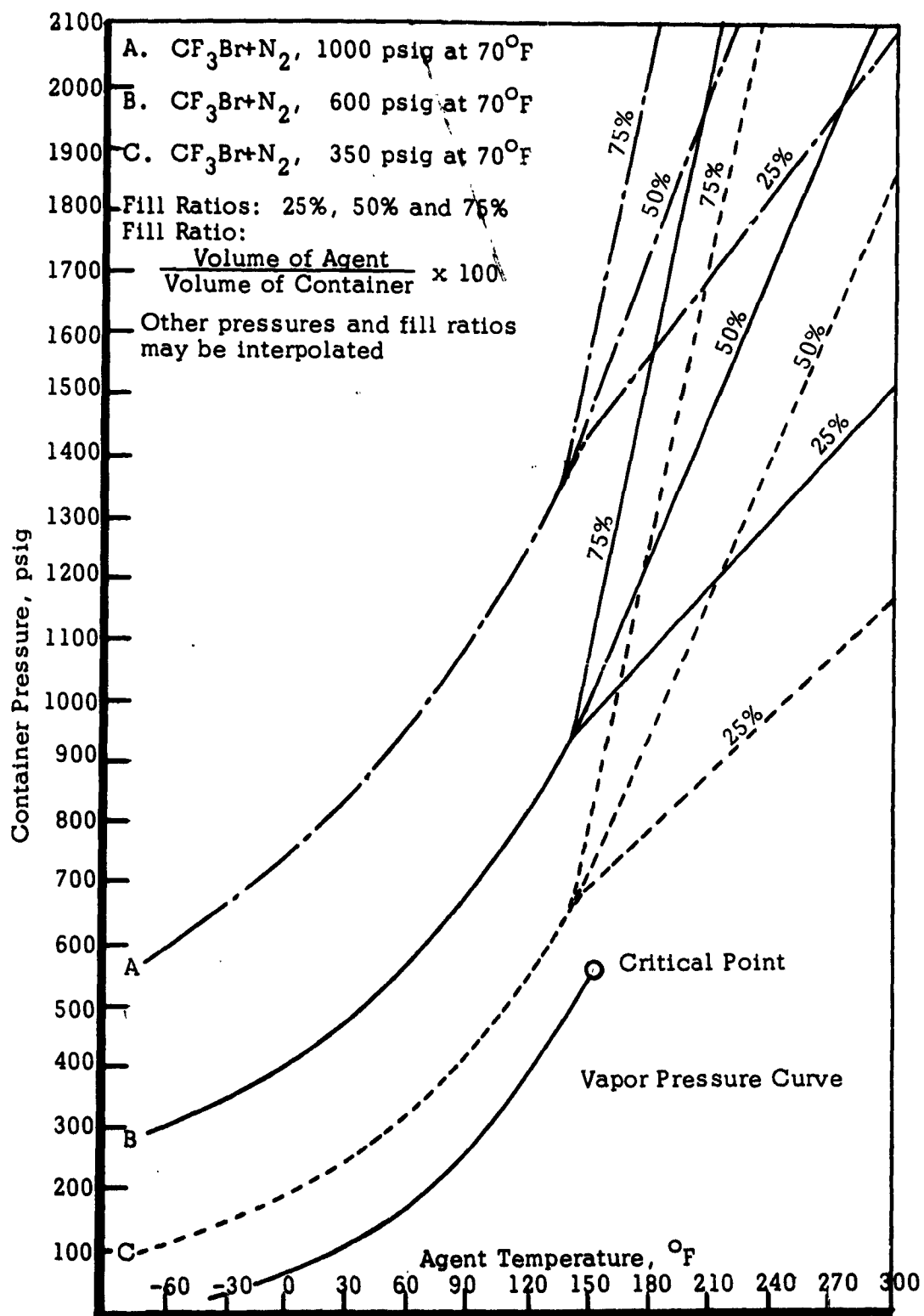
Figure 71. Container Pressures of CF_3Br and N_2 versus Temperature

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$$\Delta V_e = \frac{M_e}{R} \left[\frac{P_{e,T} V_{g,T}}{T} - \frac{P_{e,70} V_{g,70}}{530} \right] \tag{113}$$

where $\Delta V_e = V_{e,70} - V_{e,T}$

$V_{g,T} = V_t - V_{e,T}$

V_t = total volume of system

The total change in gaseous volume including both density changes and vaporization becomes:

$$V_{g,T} = V_t - \frac{\rho_{e,70} V_{e,70}}{\rho_{e,T}} - \Delta V_e \tag{114}$$

Normally these changes in liquid volume are small compared to the total volume and can be neglected as a first approximation.

The previous calculations apply only at temperatures below the critical temperature of the extinguishing agent. Above the critical temperature, an estimate of the total pressure in the container can be obtained by assuming that all of the liquid has vaporized and combined with the pressurizing gas behaves as a binary mixture of perfect gases. Such an assumption will always give a high estimate. To make such an estimate of container pressure above the critical temperature of the agent, the following equations may be used:

$$P_{g,T} = P_{g,70} \times \frac{T}{530} \times \frac{V_{g,70}}{V_t} \tag{115}$$

$$P_{e,T} = \frac{\rho_{e,70} V_{e,70} RT}{M_e V_t} \tag{116}$$

$$P_{t,T} = P_{g,T} + P_{e,T} \tag{117}$$

As an example of a calculation of $P_{t,T}$ above the critical temperature, the following conditions are assumed for CF_3Br.

$V_R = 1/4 \ V_t$ at $70^\circ R$

$P_{t,70} = 1015$ psia

Calculate P_t at 300°F (critical temperature of CF_3Br is 150°F).

$$P_{g,T} = 870 \text{ psia}$$

$$P_{e,T} = 1390 \text{ psia}$$

$$P_{t,300} = 2260 \text{ psia} = 2245 \text{ psig}$$

The pressure shown for this condition in Figure 71 is 2080 psig, which illustrates the high values resulting from the assumption of perfect gas behavior. Use of a different equation of state for the extinguishant would give a better estimate.

Other equations of state than the perfect gas law would give better estimates of the agent pressure above the critical temperature. Such equations as the van der Waals equation:

$$\left(P + \frac{a}{V^2} \right) \left(V - b \right) = RT \tag{118}$$

where
P	=	pressure
V	=	volume per mole
a	=	constant
b	=	constant
R	=	gas constant
T	=	absolute temperature

or the Dieterici equation:

$$P \ (V - b) = e^{-\frac{a}{RTV}} \tag{119}$$

can be used for estimates above the critical temperature.

The constants "a" and "b" can be obtained empirically or can be related to the critical properties of the fluid as follows:

For van der Waals equation

$$a = \frac{27R^2 T_c}{64P_c} \tag{120}$$

$$b = \frac{RT_c}{8P_c} = V_c/3 \tag{121}$$

For the Dieterici equation

$$a = 4RT_cb = 29.56P_cb^2 \qquad (122)$$

$$b = {}^{V_c}\!/_2 \qquad (123)$$

where T_c = critical temperature

            P_c = critical pressure

            V_c = critical volume per mole

      Examination of Table 32 shows that the three agents currently in use exceed 1660 psia at 500°F for an initial pressure at 70°F of 400 psia. Agents CF_3Br and $CBrClF_2$ have vapor pressures which exceed 1660 psia while the combination of CF_2Br_2 vapor pressure and N_2 pressure exceed this value. It is of interest to note that if the driver gas and agent were stored separately, a container at 400 psia at 70°F to hold the pressurizing gas would achieve a pressure of 725 psia at 500°F and the container holding the agent would achieve a pressure of only 1160 psia at 500°F. Such a dual container system would thus minimize the high pressure problem although CF_2Br_2 would still be limited by thermal stability. The use of separate containers for pressurizing gas and extinguishant complicates the system since two containers and an additional valve are required. A valve which did not permit flow of agent into the driver gas would be required and would open only when the agent pressure fell below 400 psia and the agent valve was actuated. Another possible technique to minimize the high pressure problem would be to use a container consisting of an inner cylinder holding the agent and an outer cylinder holding the pressurizing gas connected through a valve. The container system is shown schematically below.

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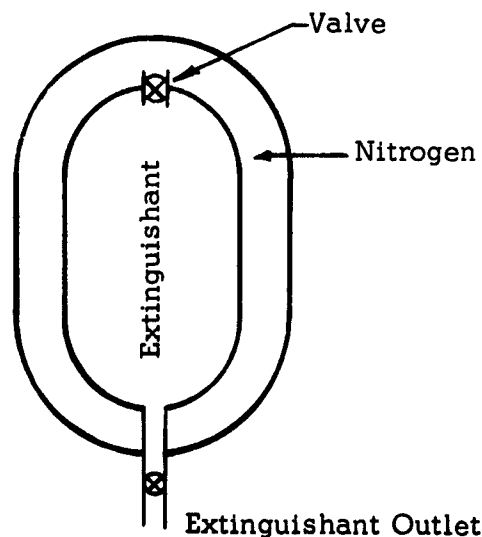
The advantage to the double container system is that the pressure differential on each metal wall is reduced. The outer shell experiences only the pressure difference between the ambient atmosphere and the pressurizing gas while the inner shell experiences only the difference between the pressurizing gas and the extinguishant. For example, using the data of Table 33, the following pressure differences would exist at 500°F and the ambient atmosphere treated as a vacuum.

Table 35. Pressure Differences on Double Extinguishant
Container 500°F

Agent	ΔP, psia	
	Inner Container	Outer Container
CF_3Br	2000	725
$CBrClF$	1375	725
CF_2Br_2	435	725

Such containers might make it possible to consider more volatile agents although the thermal stability requirements are unchanged.

Another important factor in establishing the requirements of the extinguishing system is the quantity and flow rate of extinguishant necessary to inhibit flames in a given space with and without air flow. The quantity of extinguishant required to inert a vapor-air mixture in a closed bay (no air flow) can be determined from the extinguishant concentration which prevents flammability as determined by flammability limit experiments discussed previously. Some typical data for various extinguishants have been presented in Table 31. Using CF_3Br as an example, one can calculate the minimum weight of extinguishant required by the following equation:

$$M_{e,s} = \frac{PV_e M_e}{RT} \qquad (124)$$

where $M_{e,s}$ = weight of extinguishant required, static gas

   V_e = volume of extinguishant required

   M_e = molecular weight of extinguishant

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$$T \quad = \text{ Temperature}$$

$$V_e \quad = C_v V$$

where

$$C_v \quad = \text{ peak concentration of extinguishant, volume fraction}$$

$$V \quad = \text{ volume of bay}$$

For the following conditions:

$$P \quad = 15 \text{ psia}$$

$$R \quad = 10.71$$

$$T \quad = 530^{\circ}F$$

$$M \quad = 149 \text{ for } CF_3Br$$

$$C_v \quad = .06 \text{ for } CF_3Br$$

$M_{e,s} \quad = .02V$ pounds of extinguishant as the minimum required to inert a static volume of mixture. Assuming for the moment that C_v does not change with temperature or pressure, then one can calculate M_e at other conditions by the equation:

$$\frac{(M_{e,s})_2}{(M_{e,s})_1} = \frac{P_2 T_1}{P_1 T_2} \tag{125}$$

If an air flow exists, then the volume of air flowing per second is given by:

$$\dot{V}_A = \frac{\dot{M}_A}{A} \tag{126}$$

The quantity of extinguishant required for the additional air entering the ventilated system is thus:

$$M_{e,f} = \left(\frac{M_{e,s}}{V}\right)\left(\frac{\dot{M}_A}{\rho_A}\right) \ t \tag{127}$$

The total extinguishant required is given by

$$M_e = M_{e,f} + M_{e,s} \tag{128}$$

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For the CF_3Br example calculated previously, using an air density of .074 #/ft^3 and assuming one second of flow (t = 1) or the mass flow of extinguishant (pounds per second)

$$M_e = .02 \times \frac{\dot{M}_A}{.074} \times 1 + 0.02V \tag{129}$$

$$M_e = .27 \dot{M}_A + 0.02V \tag{130}$$

The general equation for the minimum extinguishant weight thus becomes

$$M_e = \frac{PC_v M_e}{RT} \left[\frac{M_A}{\rho_A} t + V \right] \tag{131}$$

The previous paragraphs have considered the use of an extinguishing agent as a diluent. Air, of course, can also be considered a diluent if sufficient air is used to reduce the fuel concentration below the lean flammability limit.

If the volume fraction of fuel at the lean flammability limit is given by

$$L_v = \frac{V_f}{V_A + V_f} \tag{132}$$

where L_v = lean flammability limit, volume fraction of fuel

V_f = volume of fuel

V_A = volume of air

then

$$M_A = \frac{M_A}{M_f} \frac{\dot{M}_f}{L_v} (1 - L_v) \approx \frac{M_A}{M_f} \frac{\dot{M}_f}{L_v} \tag{133}$$

is the mass flow of air required to produce a limit mixture for a fuel mass flow given by $\dot{M}_f$.

where $\dot{M}_A$ = mass flow of air

$\dot{M}_f$ = mass flow of fuel

M_A = molecular weight of air

M_f = molecular weight of fuel

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and
$$\dot{M}_A = \dot{M}_f (1 - L_v) \frac{1}{L_w} \approx \dot{M}_f \frac{1}{L_w} \tag{134}$$

where L_w = lean limit, mass fraction

or
$$\dot{M}_A = \dot{M}_f \frac{1}{L_{f/A}} \tag{135}$$

where $L_{f/A}$ = lean limit, fuel-air ratio

One thus has a direct relationship between the mass or mass flow of air required to dilute a given mass or mass flow of fuel vapor since M can be replaced by M in each equation.

For a typical JP fuel with a lean limit fuel-air ratio approximately equal to 0.035, roughly 29 pounds of air would be required per pound of fuel. The air velocity required is given by:

$$V_A = \frac{\dot{M}_A}{\rho_A A} \tag{136}$$

where V_A = air velocity

ρ_A = air density

A = cross-sectional area of passage

Since the required air velocity depends on the air density, the velocity changes with pressure and temperature according to:

$$V_a \sim \frac{T_A}{P_A} \tag{137}$$

The conditions of supersonic transport cruise involve flow pressure and high temperature thus tend to require very high air velocities for dilution. Ventilation with air also aggravates the problems associated with the use of inhibitors as discussed previously.

In addition to the problem of inhibitor dilution by air flow, two other problems must be considered in the use of certain types of inhibitors. These are the possibility of ignition of the inhibitor -air mixture by hot surfaces and the possibility of reaction of the inhibitor with materials contacted during application of the agent.

Ignition temperatures of several halogenated hydrocarbon type extinguishants have been measured. Typical values of autoignition temperature are given in Table 36 (Refs 78, 79 and 28).

Table 36. Autoignition Temperatures (^{O}F) of Halogenated
Hydrocarbons

Halogenated Hydrocarbons	Autoignition Temperature, ^{O}F	
	Air	Oxygen
$CCl_3CF_2CFCl_2$	1200 *	1160 *
$CF_3CHBrCl$	1170 *	1070 *
$CF_2BrCFClCF_2CHFCl$	986 *	865 *
CCl_2FCF_2Cl	1200 *	1200 *
CF_2BrCl	1200 **	1090 **
CF_2Br_2	1200 **	1100 ** (868) ***
CF_3Br	1200 **	1215 ***
$CBrF_2CBrF_2$	1050 **	860 **
CH_2BrCl	840 ** (975) ***	690 **
CH_3Br		738 ***

* Ref 78
** Ref 79
***Ref 28

Several conclusions are evident. The ignition temperatures of the halogenated hydrocarbons all exceed the stagnation temperature associated with Mach 3 flight. Ignition by hot engine parts, if the temperature exceeds 1200°F, is not ruled out for any of the agents listed and is shown to be a possibility for several of the agents. The data of Table 36 were obtained at one atmosphere pressure, however, and higher values would be expected at altitude. Compounds containing hydrogen have lower ignition temperatures generally than fully halogenated agents but increasing the length of the carbon chain (increased molecular weight) shows a similar effect, although less pronounced.

The environment of the supersonic transport does not appear to introduce new problems with respect to extinguishing agent ignition by hot surfaces. Since the effect of reduced pressure counteracts the effect of increased temperature it does not appear that agent ignition will be a different problem in the supersonic transport than in conventional aircraft.

The use of titanium in the supersonic transport has also raised some questions concerning possible reactions with halogenated hydrocarbons. At 1300°F titanium is known to react with steam to form hydrogen and titanium dioxide (Ref 80). According to Ref 81 and Ref 82, titanium will react with carbon dioxide at 1650°F forming carbon monoxide and titanium dioxide. A definitive answer does not exist with regard to the reaction of titanium with halogenated hydrocarbons. Such a study, which would define the nature of such reactions and the temperatures at which they occur, is needed to provide a sound basis for determining the suitability of halogenated hydrocarbons as extinguishing agents in areas where titanium is used. It appears that halogenated hydrocarbons would not be suitable for extinguishing titanium fires but it is not clear that these agents would cause ignition of titanium structures if used to extinguish a hydrocarbon fire.

III. SUMMARY OF RESULTS RELATED TO SUPERSONIC TRANSPORT ENVIRONMENT

The data and discussion in the preceding text are summarized in this section with specific reference to the environment and unique problems of the supersonic transport. Wherever possible the discussion is referred to figures, tables and equations in the main body of the text to avoid duplication. Areas of specific concern are discussed in greater detail to illustrate those problems and potential solutions which are specific to the supersonic transport.

A. FUEL AND FUEL SYSTEM CHARACTERISTICS

1. Fuel Volatility

a. Typical Specification Analysis

Typical specification data with respect to volatility are presented in Table 37 for three fuels to indicate the type of data normally available.

Table 37. Analysis of Typical Jet Fuels

Test	JP-4	JP-5	JP-6
a. Distillation			
Initial Boiling Point, $^{\circ}$F	132	341	294
10% Distillation Point, $^{\circ}$F	203	394	323
30%	239	–	–
50%	310	418	370
80%	403	–	–
90%	442	461	445
95%	–	480	–
End Point, $^{\circ}$F	489	507	492
b. Gravity, $^{\circ}$API	52.7	42.9	43.6
c. Reid Vapor Pressure, psi	2.6	–	–

b. "True" Vapor Pressure

The following procedures may be used to estimate vapor pressure.

(1) From Reid vapor pressure use equation (17), page 38, to get vapor pressure at $100^{\circ}F$.
Example: In Table 37 for JP-4: Reid Vapor Pressure = 2.6
Slope at 10% point, S, estimated from:

$$\frac{t_{20} - t_{initial}}{20} = \frac{239 - 132}{20} = 5.4$$

From equation (17), page 38:

$$P_{100} = 2.85 \text{ psia}$$

(2) From reported data - see Figure 15, page 37.

c. Boiling Point

(1) Volumetric average boiling point - use equation (19), page 39.
From data of Table 37 one gets for t_v,

Table 38. Volumetric Average Boiling Point

Fuel	JP-4	JP-5	JP-6
t_v, $^{\circ}F$	316	409	370

(2) Weight average - use Figure 16 to correct volumetric average boiling point. Slope estimated from 10% and 90% points since 70% point not given.

$$\text{Slope} = \frac{t_{90} - t_{10}}{80}$$

(3) Mean average - same as above

(4) Molal average - same as above

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Table 39. Average Boiling Points for Jet Fuels

Fuel	JP-4	JP-5	JP-6
Slope	3.0	0.8	1.5
Correction (Figure 16)	-5	+10	0
Weigh Av. B. Pt, $^{\circ}$F	311	419	370
Correction (Figure 16)	-40	0	-10
Mean Av. B. Pt, $^{\circ}$F	276	409	360
Correction (Figure 16)	-45	0	-10
Molal Av. B. Pt, $^{\circ}$F	271	409	360

(5) Normal boiling point

    a.   Temperature at which vapor pressure is equal to 1 atmosphere.

    b.   If vapor pressure curve is not available calculate from known vapor pressure and equation (13), page 33, using P_2 = 1 atmosphere.

    c.   Use 10% point on ASTM distillation curve.

d. Heat of Vaporization

(1) Use equations (20) and (21), page 41.

    Example: For JP-4, $T_B \sim 203^{\circ}$F from Table 37, or Figure 15, page 37.

        From Figure 17, page 42, Mol Wt = 120 (using mean average boiling point from Table 39).

$$H_v = 22 \times \frac{663}{120} = 122 \ \frac{btu}{\#}$$

(2) From Figure 18, page 43, using 10% point for normal boiling point

2. Fuel-Air Composition

a. The volume fraction of fuel is given by:

$$F_v = \frac{P_f}{P_f + P_a} = \frac{P_f}{P_t} \qquad (138)$$

where F_v = volume fraction of fuel

P_f = vapor pressure of fuel

P_a = air pressure

$P_f + P_a$ = P_t, ambient pressure

b. The weight fraction of fuel is given by:

$$F_w = \frac{m_f}{m_f + m_a} = \frac{P_f M_f}{P_f M_f + P_a M_a} \qquad (139)$$

where F_w = weight fraction of fuel

m_f = weight of fuel

m_a = weight of air

M_f = molecular weight of fuel

M_a = molecular weight of air = 29

c. The fuel-air ratio is given by:

$$F/A = \frac{m_f}{m_a} = \frac{P_f M_f}{P_a M_a} \qquad (140)$$

and

$$F_v = \frac{F/A \left(\dfrac{M_a}{M_f}\right)}{1 + F/A \left(\dfrac{M_a}{M_f}\right)} \qquad (141)$$

$$F/A = \left(\frac{F_v}{1 - F_v}\right) \left(\frac{M_f}{M_a}\right) \qquad (142)$$

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Some typical values of F/A for conditions pertinent to the supersonic transport flight plan are presented below.

Table 40. Fuel-Air Composition for Typical Conditions

Altitude, feet	P_t, psia	T_f, °F	P_f, psia		F/A	
			JP-1	JP-5	JP-1	JP-5
Sea Level	14.7	70	.04	.01	.02	.008
		100	.10	.035	.04	.02
		200	1.10	.45	.47	.02
20,000	6.75	70	.04	.01	.04	.02
		100	.10	.035	.09	.04
		200	1.10	.45	1.14	.59
40,000	.2.72	70	.04	.01	.09	.05
		100	.10	.035	.22	.09
		200	1.10	.45	4.00	1.41
60,000	1.05	70	.04	.01	.23	.12
		100	.10	.035	.61	.23
		200	1.10	.45	--	4.87
80,000	.41	70	.04	.01	.63	.30
		100	.10	.035	1.88	.63
		200	1.10	.45	--	--

The fuel-air ratios as a function of flight plan are discussed later in connection with flammability limits.

3. Fuel Tank Vent Flow

The tank vent flow velocity is given by equations (9) and (10) on page 28. A simplified equation using the analytic form of dP/dh results in:

Some typical values of $^F/A$ for conditions pertinent to the supersonic transport flight plan are presented below.

Table 40. Fuel-Air Composition for Typical Conditions

Altitude, feet	P_t, psia	T_f, ^oF	P_f, psia		$^F/A$	
			JP-1	JP-5	JP-1	JP-5
Sea Level	14.7	70	.04	.01	.02	.008
		100	.10	.035	.04	.02
		200	1.10	.45	.47	.02
20,000	6.75	70	.04	.01	.04	.02
		100	.10	.035	.09	.04
		200	1.10	.45	1.14	.59
40,000	2.72	70	.04	.01	.09	.05
		100	.10	.035	.22	.09
		200	1.10	.45	4.00	1.41
60,000	1.05	70	.04	.01	.23	.12
		100	.10	.035	.61	.23
		200	1.10	.45	--	4.87
80,000	.41	70	.04	.01	.63	.30
		100	.10	.035	1.88	.63
		200	1.10	.45	--	--

The fuel-air ratios as a function of flight plan are discussed later in connection with flammability limits.

3. Fuel Tank Vent Flow

The tank vent flow velocity is given by equations (9) and (10) on page 28. A simplified equation using the analytic form of dP/dh results in:

$$U = 4 \times 10^{-5} \left(\frac{V}{A}\right)\left(\frac{r}{c}\right) \qquad (143)$$

where   U   = vent flow velocity, ft/sec

         V   = tank empty volume, ft^3

         A   = vent exit area, ft^2

         r/c = rate of climb, ft/sec (negative for descent indicates flow into tank)

The environment of the supersonic transport introduces no new factors into this equation.

4.   Fuel Expansion

     a.   Density Changes

Changes in density with temperature can be calculated by equation (25), page 44. The coefficient of expansion can be obtained from Figure 19, page 45, at low pressure and Figure 20, page 46, at high pressure. The coefficient of expansion, C_{ex}, is related to the ordinate of Figures 19 and 20, the multiples of volume at 60°F, m_v, by the relation

$$C_{ex} = \frac{1 - m_v}{m_v(60 - t)} \qquad (144)$$

where C_{ex} = expansion coefficient, equation (25)

         m_v = multiple of 60°F volume, Figures 19 and 20

         t   = temperature, °F

     b.   Pressure Changes

If the fluid is confined so that the volume cannot change, the change in density produces a pressure change. Within the range, 0 to 1500 psig, Figures 19 and 20, pages 45 and 46, can be used to obtain an estimate. Consider in Figure 19, a fuel with a 400°F molal average boiling point and at a temperature of 210°F which corresponds to a volume 1.1 times the 60°F volume. To achieve the same volume at 1500 psig in Figure 20, this fuel would be at a temperature of 225°F. In other words the temperature increase of 15°F caused a pressure change in this constant volume system equal to 1500 psig.

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The large pressure increase of a completely confined liquid with increases in temperature is important in establishing procedures in a hazard situation. If a damage occurs in a fluid line and valves are closed to prevent further fluid flow, it is important that the isolated system contain a free volume so that the lines are not completely filled with fluid.

Consider, for example, a fuel at $210^{\circ}F$ and a pressure coefficient of 100 psig per $^{\circ}F$ (see previous example). If such a fluid is isolated in a region with an environmental temperature of $500^{\circ}F$, the increase of fluid pressure would be in excess of 29,000 psi. The actual pressure would probably exceed this value since the pressure coefficient increases with temperature (see Figure 21, page 48).

It is essential, therefore, that shut-off valves incorporated into fluid systems be associated with an expansion volume or that the isolated system contain pressure relief valves to prevent excessive pressures due to thermal expansion of the isolated fluid. The data in Figures 19 and 20 show the required free volume to permit expansion of the liquid without excessive pressure build-up.

B.   COMBUSTION CHARACTERISTICS

1.   Oxidation

There are no temperature, pressure or composition limits for oxidation of fuel by oxygen. The rate of oxidation and associated temperature and pressure increases is a function of temperature, pressure and composition, however. The rates increase exponentially with temperature, roughly with the square of the pressure and are a maximum where the fuel and oxygen molar concentrations are approximately equal. Since the oxidation reactions below the temperature for ignition are generally fairly slow reactions, such reactions are most likely to occur during cruise. It can be seen that the pressure increases (Table 4, page 60) are relatively small at low pressure so that these oxidation reactions do not appear to be a primary hazard. Oxidation of fuel can affect the chemical nature of the fuel, however, by producing peroxides which can affect ignition temperature.

The only certain method of eliminating oxidation reactions is the complete exclusion of oxygen.

2.   Cool Flames

Cool flames can occur at low pressure and at temperatures below the normal ignition temperature at these low pressures. Such cool flames can also occur in fuel rich mixtures likely to exist during high altitude flight (see Table 4). Figure 26 shows typical cool flame regions for pentane-O_2. The data are representative of jet fuel-air mixtures since oxygen concentration

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does not greatly affect these zones and hydrocarbon type is also a secondary variable. The data of Figures 29 and 30 show typical cool flame regions for jet fuels in the pressure environment associated with the supersonic transport. It is seen that cool flames are not obtained for JP-4, JP-5 and JP-6 at any level of pressure for temperatures below 440°F and below 500°F at 60,000 feet and below 540°F at 80,000 feet.

It is shown in Table 5, page 68, that tetra-ethyl lead can eliminate the cool flame region under some conditions and in Figure 31 that certain amines can inhibit cool flame formation.

A more complete discussion of the importance of cool flame phenomena to the supersonic transport fire hazard is given in a later section.

Pressure rise associated with cool flames is small, the pressure rise increasing as the initial pressure increases. Table 6, page 69, gives some typical pressure rises associated with initial pressures in the range of interest for the supersonic transport. The pressure rise is also a function of oxygen content of the atmosphere. In the cool flame region, pressure rise can be related to oxygen content by:

$$\Delta P = a P_{O_2} \tag{145}$$

where ΔP = pressure rise, psia

P_{O_2} = partial pressure of oxygen, psia

a = constant

For the data of Figure 34, page 74,

$$P = 0.7 P_{O_2} \tag{146}$$

The use of oxygen partial pressure eliminates the variation due to total pressure.

3.   Normal Flames

The spontaneous ignition temperatures of pure hydrocarbons and several hydrocarbon fuels are listed in Table 7, page 77. No theory exists which permits the calculation of ignition temperatures so that experimental data is always required. A temperature of 440°F appears as the lowest ignition temperature for jet fuels. Normally a safety margin of 50°F is allowed in considerations of heated surface which fuel may contact indicating a maximum wall temperature of 380°F at sea-level or 1 atmosphere pressure.

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Spontaneous ignition temperature increases with pressure as shown in Figure 35, page 79, Tables 10 and 11, Page 80, and Figure 36, page 81. It is evident from Figure 36 that the ignition temperature exceeds 700°F for a wide variety of flammables at pressures below 10 psia (equivalent to an altitude of about 10,000 feet).

A temperature-altitude cross plot of the unwetted tank wall temperature for a typical flight plan is illustrated in Figure 72 along with the ignition temperature-altitude curve for JP-6. It is seen that the unwetted tank wall temperature does not reach the ignition temperature of JP-6 at sea level until altitudes in excess of 60,000 feet at which point the actual ignition temperature of JP-6 is well above 1000°F. Normal flames will thus not be initiated directly but it has already been shown that cool flames can appear. The significance of the combination of cool flame and normal flame behavior is discussed below.

4. Typical Supersonic Transport Thermal Ignition Environment

a. Main Fuel Tanks

In order to illustrate the nature of the ignition hazard associated with cool flames and the transition to normal flames, the data of Figure 29 for JP-5 have been repeated in Figure 73 along with two hypothetical descent characteristics in terms of the altitude-temperature variation. The start of the descent indicated by "S" on the figure assumes an initial condition of 80,000 feet and an unwetted wall temperature of 525°F. This condition is outside the ignition boundary for JP-5 and ignition should not occur although slow oxidation reactions cannot be ruled out.

A descent path to the left of the line originating at "S" and passing through "A" would avoid both the cool flame and normal flame ignition regions. A descent path to the right of the line defined by "S" - "A" but to the left of the line defined by "S" - "B" would involve conditions associated with cool flame ignition but not with normal flame ignition based on the combination of wall temperature and altitude. A descent path to the right of the line "S" - "B" would involve tank conditions which are within both the cool flame and normal flame ignition zones.

The interpretation of the ignition hazards associated with the descent path defined by line "S" - "B" must be considered in another manner than outlined above, however, before a complete picture of the hazards involved can be evaluated. If air is entering the tank during the descent, then it must be assumed that the cool flame is not necessarily a transient phenomenon but can exist within the tank as a stable flame. This would mean that a cool flame zone exists within the tank and, as a result of the temperature rise across the cool flame, a temperature zone exists which is at a higher level of temperature than the unwetted tank wall. This has been illustrated in Figure 73 by a broken line. The construction of this line was based on an

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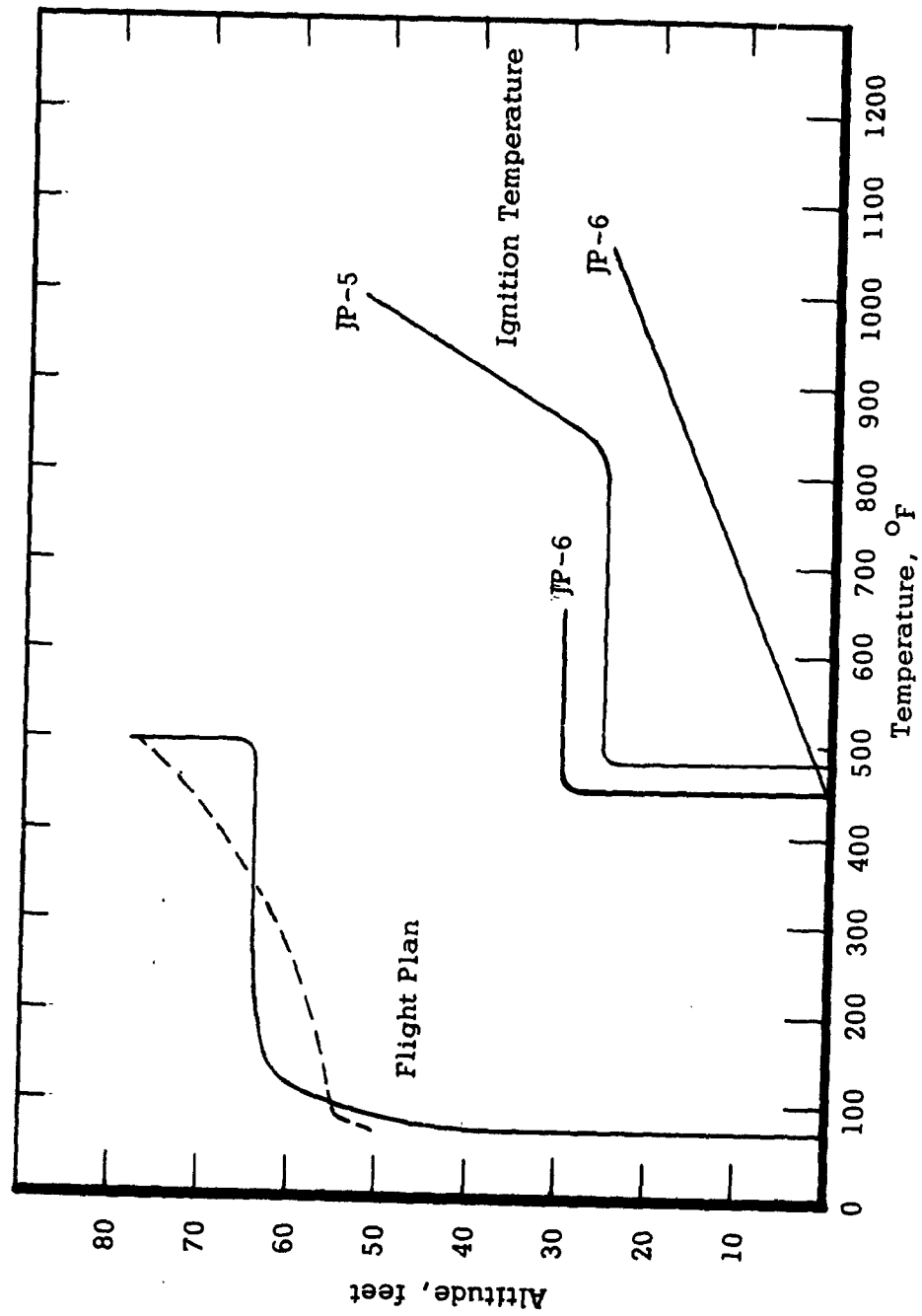
Figure 72. Relationship of JP-5 and JP-6 Ignition Temperature to Flight Plan
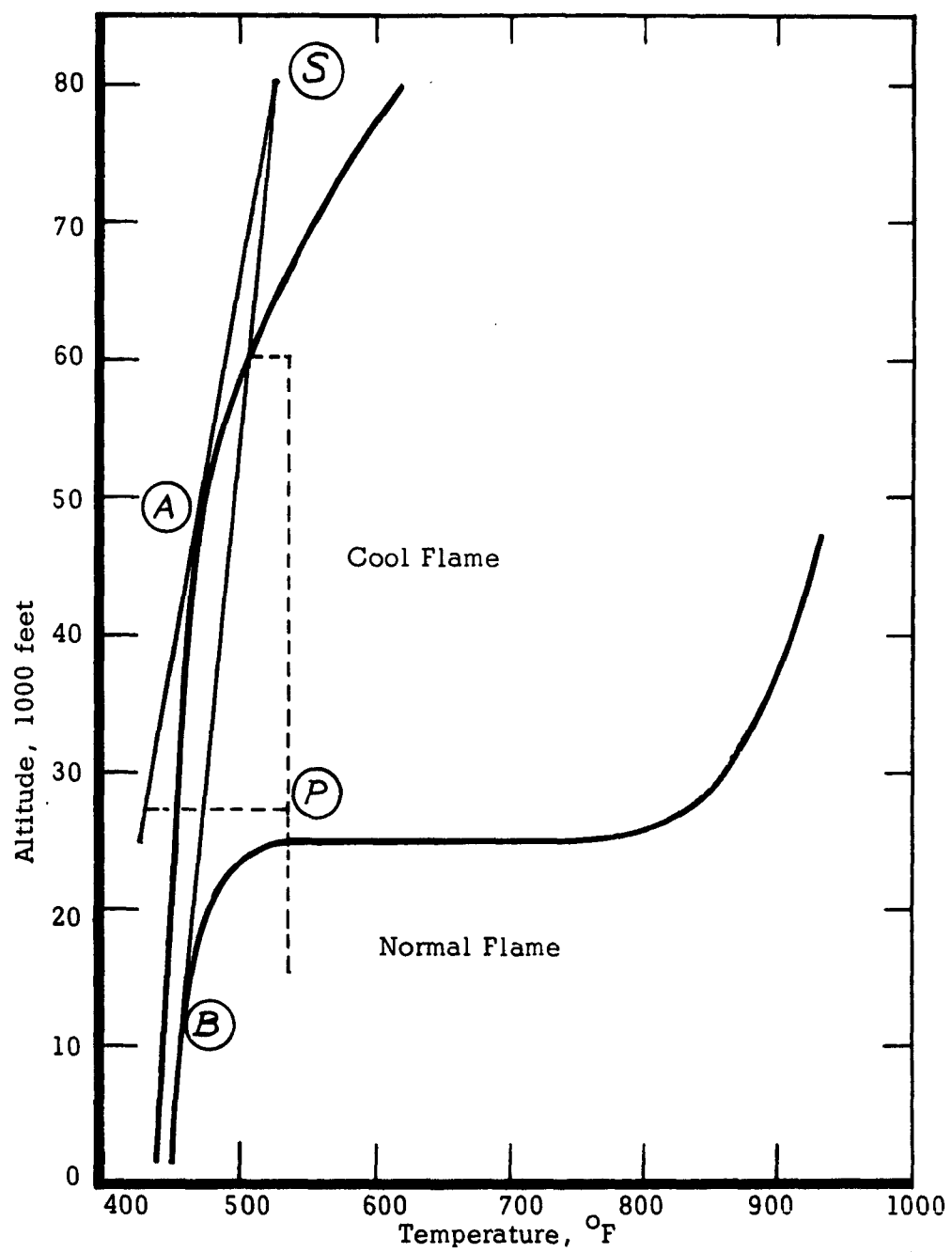
Figure 73. Spontaneous Ignition Temperature Zones for JP-5

assumed temperature rise of $250^{\circ}F$ across the cool flame. For the assumed conditions this implies a cool flame temperature of about $530^{\circ}F$, which is quite reasonable. Although the tank walls cool down during the descent defined by the line "S" - "B", a higher temperature source of ignition than the tank wall exists in the form of the cool flame. The implication of this discussion is that the formation of a stable cool flame within the tank must be avoided during a descent. If such a stable cool flame can be formed, the wall temperature is no longer the critical factor in determining the ignition of a normal flame but rather, the transition of the cool flame to a normal flame becomes the critical factor.

As indicated previously some consideration has been given to the use of a pressurized tank above 27,000 feet, corresponding to approximately 5 psia. For an unwetted tank wall temperature of $525^{\circ}F$, such a tank would correspond to an initial condition denoted in Figure 73 by "P". If sufficient air existed within the tank to permit formation of a cool flame, cool flame ignition could occur. Presumably, however, until the aircraft reaches an altitude below 27,000 feet no additional air would enter the tank. A stable cool flame could not be formed and after the cool flame reactions had ceased, a relatively inert condition would exist. The cool flame would have conserved sufficient oxygen to prevent further cool flame propagation. If air were admitted to the tank, however, cool flame ignition could re-occur unless the tank wall temperature had dropped. The dotted line in Figure 73, beginning at "P" and indicating a decreasing temperature at constant tank altitude shows the required path to prevent cool flame ignition. The tank wall temperature must fall below the cool flame ignition temperature before air is admitted to the tank.

The problem of thermal ignition relative to the supersonic transport Mach 3 flight plan is as follows. In the normal configuration, the wall temperature-altitude variations are such that thermal ignition of normal flames is not anticipated. The temperature-pressure environment is adequate to provide ignition for cool flames for some descent patterns. If, during a descent, air is introduced at a rate sufficient to form a stable cool flame, the transition to a normal flame may be possible although the tank wall temperature is below that required for normal flame ignition.

Confirmation of the possible ignition hazard during descent is reported in Ref 83 and is illustrated by the following example. The initial conditions in the tank were:

P initial	= 4 psia
T initial	= $465^{\circ}F$
Dive Rate	= 4 psi/min
P fuel	= 2 psia

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For the first two minutes of the simulated dive no adverse events were noted. At approximately two minutes after the dive had begun, the tank pressure having reached 12 psia as a result of the simulated change in altitude, a sharp rise in pressure to approximately 20 psia was noted. At the same time a temperature rise in the vapor space to 650-700°F was noted. Evidence of reaction was noted prior to the sudden increase in temperature and pressure at a pressure of about 8 psia and a temperature of the order of 470°F. It should be noted that this temperature coincides with the oxidation zone and approaches the cool flame zone at low pressure.

The evidence for reaction under almost all conditions of air admission and the existence of a continuous flame or "torching" under severe conditions represents a serious hazard problem. The most obvious solution appears to be fuel-tank inerting with the complete exclusion of air. The use of additives to the fuel may also be effective.

    b. Wing Tanks

The wing tanks represent the same type of problem but the situation may be even more severe. If the fuel in these tanks is used for take-off and climb during the initial stages of flight, the residual fuel may reach considerably higher temperatures than the fuel in the main fuselage tanks. The residual fuel thus has the greatest potential of undergoing cracking reactions and oxidation reactions, both of which could increase the ignition hazard. According to the typical flight plan, the wing tanks are emptied, except for the residual fuel, in the first 20 minutes of flight. The aircraft and its environment are still at low temperature at this time. The possibility certainly exists that the wing tanks could be emptied completely either by draining the residual fuel or pumping it into the main tanks. Once emptied, the tanks could be purged with cold air. Such a procedure would completely eliminate the hazard associated with this portion of the fuel system. Without such a procedure, or some alternative such as inerting, the aircraft carries a potential hazard. Emptying these tanks and purging them with cold air not only eliminates the fire hazard but also has the advantage of reducing the formation of deposits and gums from the exposure of the residual fuel to a high temperature environment.

A less desirable solution, but one which should be investigated if the purging process is impractical, would be to keep the wing tanks completely unpressurized so that the residual fuel would boil off and, at worst, leave a small quantity of residual vapor. If such a procedure is adopted, strong consideration should be given to the use of a special fuel in the wing tanks. Such a fuel should have reasonable volatility and a relatively low end point for its ASTM distillation characteristic. In addition this type of special fuel should be specified to contain no non-volatile residue.

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c. Leakage Areas

Most of the same factors pertinent to fuel tanks are involved in areas where flammables may contact hot surfaces due to leakage. The temperature-pressure environment and its effect on thermal ignition follow the same principles.

One of the principal safety features which can be utilized is the isolation of critical leakage areas. Such areas could possibly be inerted to minimize the possibility of ignition. Another possibility for the protection of components subject to leakage exists, however. It has been shown, Figure 37 for example, that lean mixtures require higher ignition temperatures than rich mixtures or liquid. If the components of the various fluid systems involving flammable fluids could be packaged in a manner which would provide rapid evaporation of the liquid, it is possible that ignition could be avoided. The use of a low velocity air flow to aid evaporation and dilution would also be desirable in such leakage areas.

The use of an air flow would also have some effect on the required ignition temperature as indicated in Figure 46, page 103. Even a flow of the order of 2 feet per second can increase ignition temperature by the order 200°F and, in some cases, higher. The effect of flow velocity on ignition temperature can be estimated by equation (47), page 105, where the dimensions of the heated surface are not the determining factor and by equation (50), page 105, where residence time near the heated surface is the determining factor.

d. Damage Configuration

The evaluation of ignition hazard under damage conditions requires a re-examination of the temperature-pressure environment. If the damage is of such a nature that stagnation temperature and pressure can result, then the sea-level ignition temperature appears to govern the ignition requirements. If the pressure environment resulting after damage is less than 1 atmosphere, and in particular below 2/3 atmosphere (10 psia) it appears that even Mach 3 stagnation temperature is less than the required temperature for the ignition of normal flames. Cool flame ignition is still possible, however, and the combination of a damage configuration and a rapid descent could provide the conditions discussed in connection with the main fuel tanks where a transition from cool flames to normal flames was shown to occur under certain conditions.

e. Emergency Flight Plan

The previous discussion relative to thermal ignition suggests certain emergency flight procedures to minimize the possibility of a fire hazard. The take-off and ascent portions of the flight are sufficiently like those of sub-sonic aircraft with respect to temperature and pressure that the same

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emergency procedures would apply. Once the aircraft has reached equilibrium conditions during cruise, however, the indicated emergency flight plan favors a reduction in flight Mach number to a value between Mach 1 and Mach 2 while maintaining an altitude in excess of 40,000 feet. If possible, it would be desirable to maintain cruise altitude. Speed reduction at constant altitude serves two purposes in terms of ignition environment, that of reducing temperature, reducing stagnation pressure and maintaining a low ambient pressure. Both factors reduce the possibility of ignition if a fire has not occurred and increase the possibility of extinguishing the fire without re-ignition if a fire already exists.

A reduction in altitude is not desirable since the change in ambient pressure results in the admission of air to vented regions whether these regions are vented due to damage or as a part of the normal configuration. If a reduction in altitude is required, the rate of change of altitude should be the lowest value consistent with the operating characteristics of the aircraft. Descent line "S" - "A" in Figure 73 gives a maximum temperature descent in terms of ignition hazards.

5. Hot Gas Ignition

Temperatures associated with hot gas ignition are given in Table 21 and Table 22, page 106. In general, a rough rule of thumb indicates that hot gas ignition requires temperatures approximately 2 times the normal ignition temperature (Ref 28).

Hot gas ignition is most likely to occur when jets of hot gas pass from one bay where a fire exists into a bay where flammables exist. Normal concepts of quenching (to be summarized in a subsequent section) do not apply. Openings between bays must be designed to assure that passage diameters and lengths are adequate to cool the hot gas below ignition temperature. The allowable size of individual openings as a function of wall thickness is illustrated in Figure 74 (Ref 28).

6. Electrical Ignition

The minimum electrical energy necessary for ignition of optimum hydrocarbon fuel-air mixtures is of the order of 0.22 millijoules (see Table 23, page 113). Increased temperature serves to decrease the required energy while increased pressure acts in the same direction. The change in electrical ignition energy with temperature and pressure can be approximated by:

$$\frac{E_2}{E_1} = \left(\frac{T_1}{T_2}\right)^3 \left(\frac{P_1}{P_2}\right)^{1.8} \tag{147}$$

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Figure 74. Effect of Material Thickness and Compartment Pressure Differential on Allowable Size of Openings in Fire Barriers
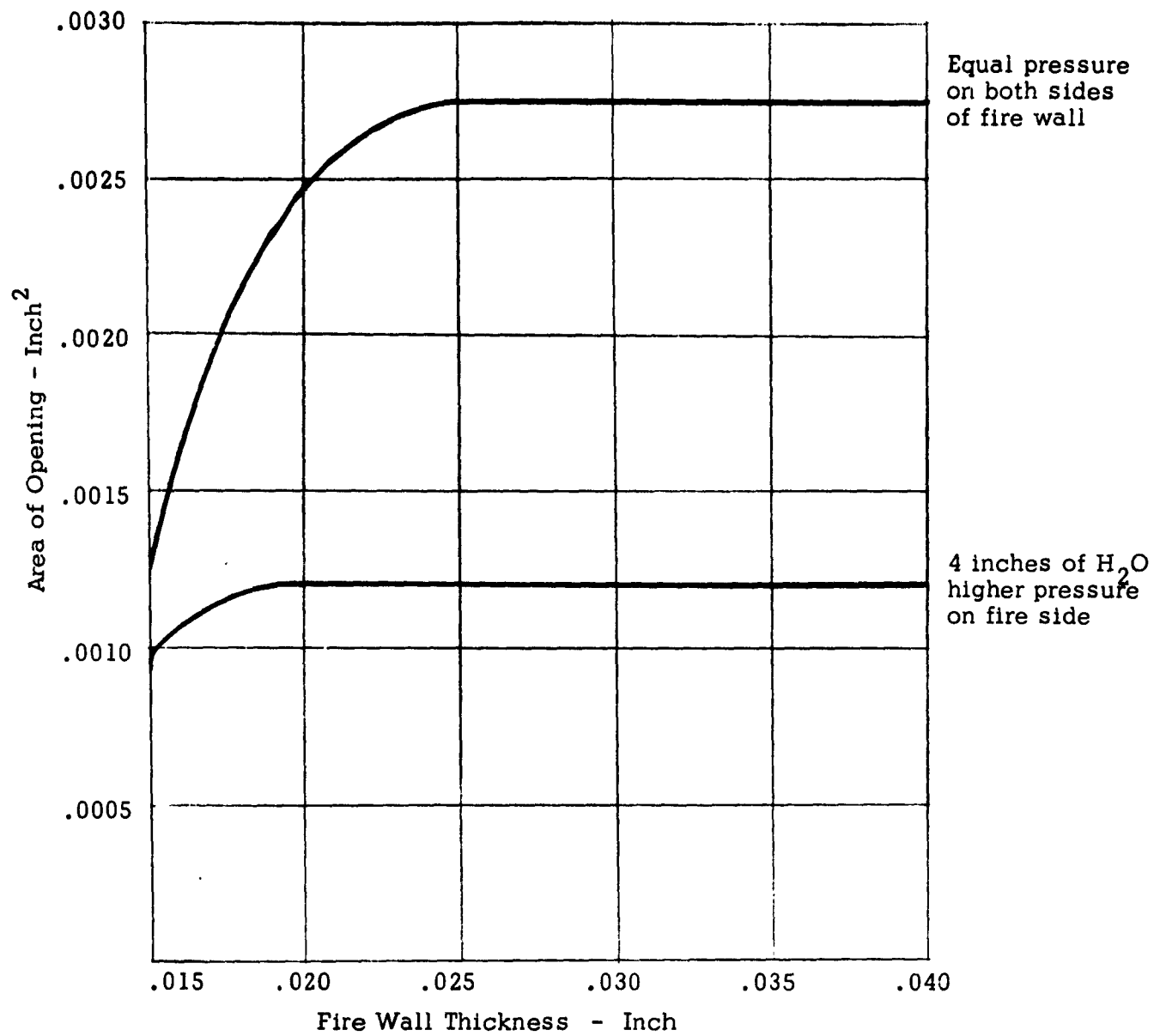
Notes: (1) Data from FAA tests
(2) Stainless Steel material was used for tests

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For $E_1 = 0.22$, $T_1 = 530^\circ F$ ($70^\circ F$) and $P_1 = 1$ atmosphere

$$E = 3.3 \times 10^7 \left(\frac{1}{T}\right)^3 \left(\frac{1}{P}\right)^{1.8} \qquad (148)$$

Some typical values of ignition energy are listed in Table 41.

Table 41. Ignition Energy at Various Temperatures and
Altitudes

$T^\circ R$	Altitude, feet	Pressure, atm.	Ignition Energy, Millijoules
530	Sea level	1	0.22
	20,000	.46	0.9
	40,000	.18	4.8
730	20,000	.46	.3
	40,000	.18	1.8
	60,000	.07	10.6
930	40,000	.18	.8
	60,000	.07	4.9
	80,000	.03	22
1130	40,000	.18	.5
	60,000	.07	2.7
	80,000	.03	12

Under the conditions likely to exist in the supersonic transport, the electrical ignition energy exceeds the sea level value.

At nearly 80,000 feet, $P_2 = .03$ atm so that for a temperature of $600^\circ F$, the required ignition energy would be approximately 15 millijoules. It appears, therefore, that the electrical ignition hazards are not increased in severity over that associated with subsonic aircraft.

7. Quenching

The minimum quenching distance between parallel plates for hydrocarbon fuels is of the order of 0.07 inches. The equivalent tube diameter obtained by using equation (57), page 118, would be 0.11 inches or an open area of 0.0094 square inches. An annular opening would permit a somewhat larger open area. The annulus dimensions can be calculated from equation (58), page 118.

The annulul dimensions which produce an equivalent quenching action to plane parallel plates (d_p = .07 inches) are illustrated by the data of Table 42.

Table 42. Quenching Dimensions of an Annulus
Equivalent to d_p = .07 Inches

a/d_a	d_a, inches	Open Area Sq. Inches
0	.11	.0095
0.1	.15	.017
0.2	.17	.022
0.3	.20	.029
0.4	.23	.035
0.5	.29	.050

a = inner diameter

d_a = outer diameter
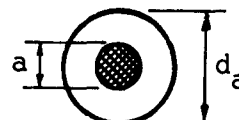
These data are pertinent to the openings in a bulkhead containing pipes or conduits. It assumes that the bulkhead temperature is the same as the gas temperature.

An approximate estimate of the effects of temperature (see Figure 53, page 122) and pressure (equation 62, page 121) can be obtained from:

$$\frac{d_{p,1}}{d_{p,2}} = \left(\frac{P_2}{P_1}\right)\left(\frac{T_2}{T_1}\right)^{1/2} \qquad (149)$$

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The temperature effect is small compared to the pressure effect so that a quenching orifice suitable for sea-level operation is likely to be suitable over the complete range of supersonic transport operation. Some typical values are listed in Table 43. The quenching distances associated with likely conditions to be encountered in the supersonic transport exceed the sea-level value.

Since flame arrestors operate as quenching channels, it appears that locations which benefit from protection by flame arrestors in subsonic aircraft would be similarly benefitted in supersonic aircraft. Since the aircraft must operate at sea-level, the flame arrestor channels would be designed on the basis of sea-level quenching distances.

Table 43. Quenching Distance at Various Temperatures and Altitudes

$T^\circ R$	Altitude, feet	Pressure, atm	Quenching Distance d_p, inches
530	Sea level	1	.07
	20,000	.46	.15
	40,000	.18	.39
730	20,000	.46	.13
	40,000	.18	.33
	60,000	.07	.86
930	40,000	.18	.29
	60,000	.07	.76
	80,000	.03	1.77
1130	40,000	.18	.27
	60,000	.07	.68
	80,000	.03	1.60

8. **Flammability Limits**

Flammability limits for pure hydrocarbons and jet fuels are listed in Table 27, page 126. The lean limit fuel-air ratio for most fuels is 0.035 and the rich limit is of the order of 0.22. The variations of the lean and rich limit volume fractions is due principally to difference in molecular weight. Lean and rich limit concentrations can be estimated from equations (63), (64), (65) and (66).

Outside the region where wall quenching affects flame propagation, the flammability limits appear independent of pressure. The assumption of no pressure dependence on limit concentration is a fairly good rule for the lean limit and is less certain for the rich limit since the nature of the flame varies with pressure in rich mixtures. Nevertheless, assuming no pressure dependence serves as a useful conservative approximation.

The effect of temperature on flammability limits is small. Approximate variations can be obtained from equations (67) and (68), page 129.

In order to illustrate the significance of the flammability limits with respect to the supersonic transport, a F/A ratio-altitude map at $70^\circ F$, $100^\circ F$ and $200^\circ F$ fuel temperature for JP-6 has been plotted in Figure 75. The lean and rich limits at $70^\circ F$ and $500^\circ F$ have been indicated on the figure.

During take-off and ascent, the fuel temperature remains at close to $70^\circ F$ to an altitude of about 60,000 feet. The fuel-air ratio for JP-6 is below the $70^\circ F$ lean limit to about 35,000 feet. A more volatile fuel such as JP-1 which has a $70^\circ F$ F/A curve corresponding to the $100^\circ F$ curve for JP-6 would have shown flammable compositions at about 15,000 feet. By the time the fuel has reached a temperature of $100^\circ F$, the aircraft has attained an altitude of 70,000 feet and the fuel-air ratio is above the rich limit. For JP-6 a flammable mixture exists between 35,000 feet and 70,000 feet. Below 35,000 feet the equilibrium fuel-air ratio is below the lean limit and above 70,000 feet above the rich limit. During the cruise portion of the flight the fuel-air ratio is above the rich limit.

The pattern during descent is strongly dependent upon the rate at which the fuel cools. If the fuel remains warm at $200^\circ F$, a flammable mixture occurs only between 10,000 feet and sea level. If the fuel cools, however, a greatly extended flammable range could exist, possibly similar to the ascent pattern.

It appears that any fuel of acceptable volatility for minimum boil-off during flight will still show rich fuel-air ratios during cruise due to the low ambient air pressure. Such a fuel will produce flammable mixtures during the middle portion of the ascent and portions of the descent depending upon the rate of cooling of the fuel. It seems quite likely that flammable fuel-air ratios will exist at altitudes of 10-20,000 feet associated with high lightning incidence.
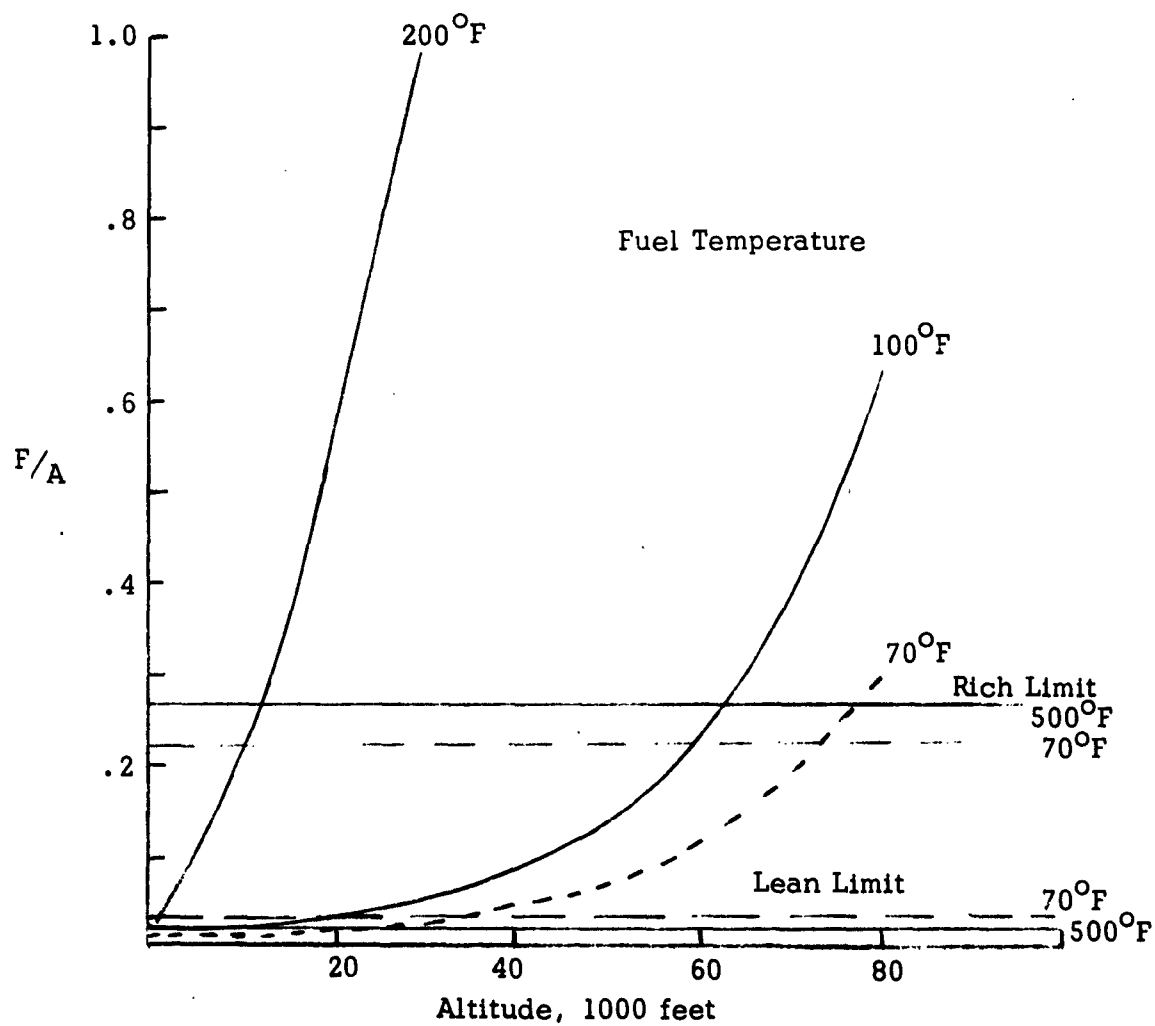
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Figure 75. Fuel-Air Ratio as a Function of Altitude and Fuel
Temperature for JP-6

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9. Flame Propagation

a. The variation of burning velocity with equivalence ratio can be represented by equation (69), page 132. A maximum burning velocity exists at a fuel-air ratio slightly rich of stoichiometric.

b. Burning velocities for hydrocarbons are listed in Table 29. Hydrocarbon fuels show a maximum value of 1.2 ft/sec at an equivalence ratio of $= 1.1$.

c. Pressure has only a mild effect on burning velocity and for many purposes it is a reasonable estimate to assume no change with pressure. A more precise estimate shows an increase in burning velocity with a decrease in pressure. Temperature has a pronounced effect on burning velocity, increases in temperature producing increases in burning velocity. The combined effects of temperature and pressure can be estimated by:

$$\frac{U_{f,2}}{U_{f,o}} = \left[0.25 + 2.6 \times 10^{-6} \, T^2\right] \, P^{-1/3} \qquad (150)$$

where
$U_{f,2}$ = burning velocity at temperature T, pressure P

$U_{f,o}$ = burning velocity at $537^{O}R$, 1 atmosphere

T = temperature, ^{O}R

P = pressure, atmospheres

d. Dilution with nitrogen reduces burning velocity as described by equation (72), page 138. For nitrogen dilution, the burning velocity was zero for a mixture containing 12% oxygen.

e. Turbulence causes an increase in flame velocity. The magnitude of the increase can be estimated from equations (80) and (81), page 140. A value of 20-30 ft/sec probably represents the maximum rate of propagation of a flame in a tube without the use of flame holders, at sea-level temperature and pressure. Equation (150) can be used to estimate the effects of temperature and pressure on turbulent flame propagation rate.

f. The use of bluff body flame holders can permit stabilization of flames at velocities in excess of 200 ft/sec at sea-level temperature and pressure. The blow-off velocity is a function of obstacle dimensions as shown by equations (82) and (83), page 143.

At constant Reynolds number the effect of pressure and temperature on blow-off velocity can be represented by:

$$U_{bo} \sim p^{1.8} \, e^{-\frac{36,000}{T}} \qquad (151)$$

where   P   = pressure, atmosphere

       T   = temperature, $^{\circ}R$

g. The blow-off and flashback characteristics of flames from the ends of open tubes (Bunsen type flames) can be represented by:

$$U_{bo} = \left[100 + 4.5 \times 10^{-3} \, T^{1.9} \right] P \qquad (152)$$

$$U_{fb} = \left[100 + 1.15 \times 10^{-9} \, T^{4.2} \right] P \qquad (153)$$

These equations can be used to estimate the velocities of flashback and blow-off of a flame initiated at the exit of a vent line.

10. Extinguishing of Flames

The relative extinguishing effectiveness of a large number of halogenated hydrocarbons is summarized in Tables 31, 32 and 33. Several problems arise with respect to the use of such compounds for supersonic flight fire applications. The extinguishant must be thermally stable at likely storage temperatures, must not produce excessive pressures during high temperature storage, must possess acceptable viscosity for low temperature applications, must have an extinguishing effectiveness comparable to presently used extinguishants, must not react explosively with materials contacted. Possible candidate extinguishing agents are summarized in Table 33. These are characterized by a higher molecular weight than current extinguishants to reduce vapor pressure at high temperature. The low temperature viscosity of such agents tends to be higher than current agents, however, which could limit the rate of application of these agents at low temperature conditions.

Equations for the calculation of system pressure combining the vapor pressure of the fluid and the pressure of a driving gas are presented on pages 168 and 169. Below the critical temperature of the fluid, system pressure can be estimated by:

$$P_{t,T} = P_{e,T} + P_{g,70} \times \frac{T}{530} \qquad (154)$$

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where $P_{t,T}$ = system pressure at T^OR

$P_{e,T}$ = extinguishant vapor pressure at T^OR

$P_{g,70}$ = driver gas pressure at 70°F (530°R)

T   = temperature, ^{O}R

Above the critical temperature, equations (115-117), page 171, can be used to estimate system pressure.

It has been shown that separation of extinguishant and driver gas in separate containers can lead to reduced pressure levels in each container. Use of a gas generator such as a pyrotechnic for pressurizing the system would also lead to reduced system pressures during storage.

The possibility of reactions between halogenated hydrocarbons and titanium should be investigated to determine whether such agents are suitable in areas containing titanium.

The minimum required flow rate for extinguishant can be estimated by equation (131), page 176. The flow rate requirements for dilution by air can be estimated by equation (133), page 176, and equations (134) and (135), page 177.

IV. SUGGESTED RESEARCH PROGRAM

The study of fire hazards pertinent to the supersonic transport has involved a summary of existing knowledge on fire hazards and specific application to the environment of the supersonic transport. During the course of this study certain voids in existing knowledge became evident. The following research program is directed toward obtaining some of the required additional knowledge directly related to the problems of the supersonic transport. Many other problems of a fundamental nature were also evident during the course of the study but, since these problem areas were not specifically related to the supersonic transport, these problems have not been included in the suggested research program.

For convenience in presentation, the problems have been grouped into major problem areas, each of which is discussed separately.

A. COMBUSTIBLE AUTOIGNITION UNDER STATIC CONDITIONS

Although considerable work is reported in the review of the fire hazard problem pertinent to the supersonic transport on the subject of autoignition of combustibles under static conditions, some voids in current knowledge exist which are the result of the specific environmental conditions of the supersonic transport or which are related to new approaches of minimizing the ignition hazard under the conditions existing during a typical supersonic transport flight plan. Each of the following problems falls under the general heading of combustible autoignition under static conditions.

1. Effect of Fuel Temperature on Autoignition Temperature

In the standard ASTM type autoignition temperature determination, a combustible liquid at room temperature is injected into a heated cup, and cup temperature at which ignition occurs is recorded. In a few experiments with combustibles normally gases at room temperature, the combustible has been pre-cooled to produce a liquid which is then injected in the conventional manner. In some cases where the combustible is normally a solid at room temperature the material has been melted to form a liquid which is then injected into the heated cup. The effect of the temperature of the injected combustible on autoignition temperature has not been investigated, however. For most fire hazard studies in the past the temperature of the combustible has not been an important variable. In the case of the supersonic transport, however, the fuel, oil and hydraulic fluid may exist at temperatures in excess of 200°F under normal storage conditions and in excess of 500°F in certain areas within the engine compartment. In order to assess the ignition hazard it is essential to know the effect of combustible temperature on the autoignition temperature. At the present time, even the direction of the change in autoignition temperature with increasing combustible temperature is not known.

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An investigation should be conducted to determine the effect of fluid temperature on autoignition temperature.

2. Effect of Thermal Degradation and Oxidation on Autoignition Temperature

During the course of a typical supersonic transport flight plan the fuel is exposed to a temperature in excess of 200°F and may be exposed to varying concentrations of oxygen and during the cruise portion of the flight to a relatively high ozone concentration. The results of such exposure of the fuel to high temperature and possibly on oxidizing atmosphere could lead to chemical changes which would affect the autoignition characteristics of the fuel. These changes and their effect on autoignition temperature cannot be predicted at the present time. The presence of chemical species resulting from exposure of the fuel to high temperature, oxygen and ozone could change the autoignition temperature and affect the fire hazard. It would be unreasonable to attempt to classify all of the possible reactions and reaction products which could occur. A more direct set of experiments simulating specific environmental conditions associated with the supersonic transport is recommended to determine the effect of pre-reaction or oxidation on autoignition temperature.

3. Effect of Surface Characteristics on Autoignition Temperature

The likely materials of construction for various areas within the supersonic transport where flammables may exist does not indicate that any unusual surface effects on autoignition temperature should be expected. The objective of the study of surface effects on autoignition temperature suggested here is to determine whether surface treatment can be effective in reducing the ignition hazard. In order to determine whether surface treatment can minimize ignition hazard, it is suggested that a study be made to compare various typical surface treatments as to their influence on autoignition temperature.

4. Cool Flame Ignition and Stabilization Study

Cool flame ignition and stabilization under environmental conditions associated with the supersonic transport should be investigated with emphasis on the effects of temperature, pressure, fuel type and inhibitors on cool flame ignition and the conditions of transition from cool flames to normal flames.

B. COMPONENT ISOLATION

Certain components represent a major part of the fire hazard because of the possibility of leakage of combustible during operation. Almost every fluid system contains seals, gaskets and joints which can be the source of combustible material if a leak should develop. While such leaks do occur

in fluid systems on conventional aircraft, the ignition sources are limited and efforts are made to separate such components from likely ignition sources such as hot engine parts. In the case of the supersonic transport, however, where many exterior and interior surfaces may exceed the auto-ignition temperature of specific fluids, such isolation from ignition sources may not be possible. It is conceivable, however, that some of the characteristics of the autoignition process can be utilized to minimize the hazard due to small leaks. It is recommended that a program to study component isolation techniques to minimize autoignition be initiated.

C.   FIRE INHIBITION STUDIES

1.   Effect of Inhibitors on Ignition Temperature

Several areas of knowledge pertinent to the inhibition of ignition and of flames are unique to the supersonic transport environmental conditions. Data required to assess the potential of inhibitors under these unique conditions is not available and is essential before an evaluation of the use of inhibitors can be made. Some of the problems unique to the supersonic transport, for example, the possible existence of cool flame reactions are more easily attacked by the use of inhibitors than the normal flames associated with conventional aircraft fire hazards. While the use of additives and inhibitors is often ruled out because of other system considerations including weight of the inhibitor and application system, effects of inhibitor on engine performance and possible corrosive effects of inhibitors, a proper evaluation of the use of inhibitors should be made to determine whether a practical application does exist.

2.   Inhibitor Reactions with Materials

The in-flight extinguishant and inhibitor systems currently in use employ halogenated hydrocarbons as the inhibiting or extinguishing agent. Evidence exists in the literature that these materials may react with titanium. It is not known, however, whether such reactions introduce an additional fire hazard. These same materials react with aluminum and magnesium yet these extinguishants have been used successfully in current aircraft. While the halogenated hydrocarbons are not effective in extinguishing a metal fire once it has started, they do not by themselves initiate such a fire for presently used materials. It is necessary to determine experimentally whether the same situation exists for titanium or whether the application of halogenated extinguishing agents to hot titanium can cause burning of the titanium to be initiated.

D.   EXTINGUISHANT SYSTEM STUDIES

Methods of packaging extinguishing agents and of application of a driver gas should be investigated in an effort to obtain adequate high temperature storage and application characteristics without sacrificing low temperature efficiency.

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